

**Batteries for Advanced
Transportation Technologies
(BATT) Program
for
Electrochemical Energy Storage
4th Quarter Report
FY 2003**



Ernest Orlando Lawrence
Berkeley National Laboratory
1 Cyclotron Road, 70R0108B, Berkeley CA 94720-8168
(510) 486-4636; fax: (510) 486-4260

November 21, 2003

Mr. Tien Q. Duong
5G-030, EE-32
Forrestal Building
U.S. Department of Energy
Washington D.C. 20585

Dear Tien:

Here is the fourth-quarter FY 2003 report for the Batteries for Advanced Transportation Technologies (BATT) Program. This report and prior Program reports can be downloaded from <http://berc.lbl.gov/BATT/BATT.html>.

Sincerely,

Frank McLarnon
Manager
BATT Program

cc:	J. Barnes	DOE/OFCVT
	D. Howell	DOE/OFCVT
	R. Kirk	DOE/OFCVT
	V. Battaglia	ANL
	K. Abbott	DOE-Oakland

LBID-2490

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT) PROGRAM

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BATT TASK 1

CELL DEVELOPMENT

TASK STATUS REPORT

PI, INSTITUTION: K. Striebel, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Cell Fabrication and Testing

SYSTEMS: Low-cost Li-ion and high-power Li-ion

BARRIER: Inconsistent evaluation of the merits of candidate novel materials.

OBJECTIVES: The primary objective is to benchmark the performance of new materials for low-cost and high-power Li-ion cells.

APPROACH: The testing of novel materials in a standard cell with preset protocols will provide the necessary link between the invention of novel battery components and the diagnostic evaluation of failure modes, and will accelerate the development of a battery-powered EV. Novel components will be developed in BATT Program Tasks 2, 3, and 4 (anodes, electrolytes, and cathodes) for baseline liquid and gel electrolyte chemistries. These components are incorporated into a standardized cell, and then tested using a consistent protocol to determine cell capacity, energy, power, and lifetime characteristics. Tested cell components are then delivered to appropriate investigators involved with BATT Program diagnostic projects. Fabrication of baseline polymer-electrolyte cells is carried out in BATT Program Task 3.2.

STATUS OCT. 1, 2002: The analysis of capacity and power fade mechanisms for Li-ion cells with Gen 2 materials was completed in coordination with the ATD Program. The initial benchmarking of the low-cost Li-ion cell with LiFePO_4 and natural graphite in liquid and gel electrolyte was completed.

EXPECTED STATUS SEPT. 30, 2003: Efforts on the low-cost Li-ion baseline cell will be focused on LiFePO_4 cathodes, various gel electrolyte components applied to Celgard separators, and the evaluation of the available natural graphites. Characterization of LiFePO_4 materials prepared *via* different synthetic processes will be compared. Electrode compositions will be optimized for electronic and ionic conductivity with the aid of collaborative modeling studies (J. Newman and A.M. Sastry). New materials for the base line cells will be evaluated including, doped LiFePO_4 , $\text{Li}(\text{Ni},\text{Mn})\text{O}_2$, $\text{Li}_{0.44}\text{MnO}_2$, and intermetallic anodes.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES: (a) Benchmark the performance of the $\text{LiFePO}_4(\text{UdM})/\text{natural graphite}$ cell with liquid electrolyte - December 2002. (b) Compare performance of LiFePO_4 from different sources - May 2003. (c) Evaluate cycle performance and power capability of the LiFePO_4 / gel polymer electrolyte / natural graphite cell - August 2003.

PROGRESS TOWARD MILESTONES

Benchmarking of the LiFePO₄/natural graphite Li-ion cell with liquid and gel electrolyte, (Milestones a and c)

The room-temperature performance and cycle life of two LiFePO₄(U. d'Montreal) cathode/natural graphite anode cells have been benchmarked against the USABC goals as shown in Table 1, thus completing milestones 1 and 3. The first cell contains an SL-20 (Superior Graphite) anode, a Celgard separator and a liquid electrolyte (1M LiPF₆/EC-DEC). The second cell contains a HQ purified spherical natural graphite (SNG20) anode and a gel separator with 1.5M LiBF₄- EC:γ-Butyrolactone (1:3) (see Zaghib).

Table 1 Gap Chart for LiFePO₄/NG Low-Cost Baseline Cell

USABC Goals	Units	Mid-Term	Long-Term	HQ Gel	LBNL Liq.
Power Density ¹	W/l	250	600	523	2852
Specific Power, Dischg	W/kg	150	400	282	1018
Specific Power, Regen ²	W/kg	75	200	576	1788
Energy Density	Wh/l	135	300	89	150
Specific Energy	Wh/kg	80	200	48	54
Cycle Life ³	cycle	600	1000	222	200
Cell Weight	mg/cm ²			27	44
Cell Volume	cm ³ /cm ²			0.011	0.016
Theor. Capacity	mAh/cm ²			0.82	1.3

18s, at 80% DOD, 2 10s at 20% DOD, 3 cycles to 20% capacity loss during C/2 (100%DOD) cycling

The calculation of the cell power was discussed in the previous report. The ASI of the liquid cell was about 44 Ω-cm² compared to about 250 Ω-cm² for the gel cell. Both cathodes contain carbon-coated current collectors. However, the LBNL current collector is significantly rougher than that used by HQ. This appears to yield significantly lower contact resistances between the active later and the Al. The ASI in the liquid cell is also lower because of the higher conductivity of both the separator and the electrolyte. The cycle-life of both cells is about 200 cycles, corresponding to a capacity fade rate of 0.1%/cycle, during C/2 cycling. Electrochemical diagnostics reveal that this is due to a side-reaction in the cell: possibly the dissolution and reformation of the SEI layer on the surface of the graphite. For the different sources of natural graphite, this reaction was found to increase in the order Mag-10 (Hitachi) < SNG20 (HQ) < SL-20 (Superior Graphite). Several methods for improving the stability of the anode SEI on the SL-20 were examined, though none successfully reduced the rate of capacity fade in the pouch cell. More diagnostic analysis of the anodes will be necessary to further understand the source of the instability.

Comparison of LiFePO₄ from Different Labs

A performance comparison of cathodes prepared from six different sources of LiFePO₄ has been carried out with the aid of a computer model (see Srinivasan/Newman) to normalize for the inevitable differences in active material loading and cathode porosity. Fitting of the variable-rate discharge data to determine two particle sizes and a matrix conductivity for each LiFePO₄ cathode revealed that the HQ cathode showed the best high-power performance due to the highest solid-phase conductivity. Moderate-rate utilization of the active materials was best for the MIT cathode, due to its extremely small and narrow particle size distribution. All of the LiFePO₄ cathodes showed excellent capacity stability when cycled at C/2 against a Li counter electrode.

TASK STATUS REPORT

PI, INSTITUTION: T.J. Richardson, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cell Development - Materials Characterization, Overcharge Protection, Cathode Development

SYSTEMS: Low-cost, high-energy Li-ion

BARRIER: Short lithium battery lifetimes, inadequate capacity.

OBJECTIVES: Support cell development through structural characterization of active electrode components before, during, and after cycling. Investigate inexpensive, self-actuating overcharge protection mechanisms. Synthesize and evaluate alternative electrode materials.

APPROACH: Address primary causes of capacity and power fading by correlating them with changes in the composition and structure of electrode active materials. Techniques employed include x-ray diffraction (XRD), vibrational spectroscopy, and electroanalytical testing. Develop an internal overcharge protection mechanism based on an electrolyte or separator component that will internally short an overcharged cell. Discover improved cell systems through a limited program of synthesis and evaluation of alternative components.

STATUS OCT. 1, 2002: Phase transformations and accumulation of decomposition products (if any) in cycled electrodes from BATT Program Task 1.1 have been identified and correlated with cell performance characteristics. Efforts to assess the utility of electroactive polymers for overcharge protection in Li-ion batteries are ongoing. Some potentially useful new low-cost, high-capacity electrode materials have been prepared and evaluated.

EXPECTED STATUS SEPT. 30, 2003: Composition and structural analyses of BATT Program Task 1.1 electrodes will have contributed to our understanding of the failure and degradation modes in the baseline systems. The switching behavior of electroactive conducting polymers incorporated in Li-ion cells will have been characterized, and an assessment of their potential for providing overcharge protection will be underway. Additional new cathode materials will have been prepared and evaluated.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Construct and test an overcharge protection device utilizing an electroactive conducting polymer. (July 2003). Milestone achieved.

PROGRESS TOWARD MILESTONE

We have shown that electroactive polymers whose conductivity depends upon their state of charge can provide substantial overcharge protection in lithium batteries. Using well-characterized thin films of these polymers, we were able to visualize the potential profile across a separator containing the polymer. This, in conjunction with a calculational model developed by K. Thomas and J. Newman based on our conductivity vs. potential measurements, demonstrated the ability of the polymer to adjust its conductance to the load applied. The result is a reversible, self-actuating, low-resistance internal shunt that allows overcharge currents to pass through a cell without damaging the components. The discharge capacity is maintained after overcharging, so that other cells in a high-voltage stack may operate normally.

The initial proof of concept used Li-TiS₂ cells containing separators modified by solution deposition of 0.4 mg/cm² of poly-3-butylthiophene. The potential of an unprotected cell rose rapidly at the end of charge to more than 4V, and the subsequent discharge capacity was severely reduced. In a protected cell, the cell potential rose only to about 3.2 V and held at this value indefinitely. The discharge capacity of the protected cell was preserved, and its behavior under normal cycling conditions was largely unaffected by the small amount of polymer required. We have recently extended the onset potential for the internal short through the use of different polymers and structural modifications to about 4.0 V. This has allowed us to demonstrate overcharge protection for 3 V LiMnO₂ and 3.5 V LiFePO₄ cells. We are confident that further improvements will lead to protection for 4 V LiCoO₂ and LiNiO₂ cells.

Our approach to the development of new cathodes has been to incorporate structures known to impart stability at high states of charge in iron, manganese, or other metal oxides with appropriate theoretical capacities. The redox stability and safety of the BATT baseline electrode LiFePO₄ (178 Ah/kg) led us to investigate phosphate-containing oxides such as Fe₃O₃PO₄, an iron (III) compound easily prepared by solid-state reaction in air, with a theoretical capacity of 259 Ah/kg. Another iron (III) phosphate, Fe_{1.2}PO₄X, where X is F, OH, or H₂O was synthesized by a hydrothermal method, and showed good cyclability in a single-phase system, Li_yFe_{1.2}PO₄X, with x up to at least 1. Structural characterization of this system has been completed. Substitution of titanium for iron gave a material with good capacity and cyclability, but a reduced discharge potential. Current efforts focus on manganese substitution in this structure and on other manganese phosphates.

TASK STATUS REPORT

PI, INSTITUTION: K. Zaghib, Hydro-Québec (IREQ)

TASK TITLE - PROJECT: Cell Development - Research on Lithium-Ion Polymer Batteries Utilizing Low-Cost Materials

SYSTEMS: Low-cost Li-ion

BARRIER: High cost of Li-ion batteries

OBJECTIVES: (a) To fabricate Li-ion polymer cells (4 cm² area) using cell chemistries proposed by DOE. Cells (50% of the total cells) will be sent to LBNL for testing. (b) To investigate interfacial phenomena at the anode/separator and cathode/separator in Li-ion polymer cells. (c) To determine the cycle life and self-discharge rates of Li-ion polymer cells at different temperatures (55°C to 0°C). (d) To synthesize low-cost graphite anodes and LiFePO₄ cathode materials for Li-ion polymer cells.

APPROACH: Our approach is to synthesize and coat electrodes (both anode and cathode) with low-cost materials, and use these materials to assemble prismatic cells. Additional work will be focused on gel polymers, as well as studies of pressure effects and interfacial phenomena at the polymer/electrode interfaces.

STATUS OCT. 1, 2002: Studies were completed on the effect of different amounts of conductive carbon (1% to 15%) on the performance of LiFePO₄ electrodes. The results indicated that 6% carbon added to LiFePO₄ provides a good compromise for energy and power, while still achieving a reversible capacity of 65% at 2C rate and 62% at 3C rate. The effect of solvent mixture and the type of Li salt on the performance of Li-ion polymer cells were determined. The electrochemical performance of a Hydro-Québec (HQ) solvent (TESA) mixed with EC (3/1) was comparable to GBL-EC (3/1). Thirty cells were provided to LBNL in FY 2002 for evaluation.

EXPECTED STATUS SEPT. 30, 2003: Coating of cathodes based on LiFePO₄ with different ratios of conductive carbon (from 3 to 15 wt%) will be completed. The investigation of phenomena at the cathode/separator interface in Li-ion/polymer cells containing LiFePO₄ by *in situ* SEM will be ongoing. Analyses of the effects of carbon-coated LiFePO₄ cathode materials with different particle sizes on Li-ion polymer cell rate capability and cycle life will be ongoing. Fabrication of Li-ion/polymer cells (4 cm² area) using cell chemistries proposed by DOE will be complete, and 50% of the total cells will have been sent to LBNL for testing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10-year life, < 20% capacity fade.

MILESTONES: (a) Production of 60 Li-ion polymer cells (4 cm² area) by using highly viscous electrolyte based on GBL (γ -butyrolactone), TESA (tetraethylsulfamide), or mixed electrolytes will be completed by March, 2003, with 50% of the total cells sent to LBNL. (b) Impedance and *in situ* SEM investigations of phenomena at the anode/separator and cathode/separator interfaces in Li-ion/polymer cells will be completed by May 2003. (c) Synthesis of low-cost carbon-coated LiFePO₄ cathode material for Li-ion/polymer cells will be completed by August 2003.

PROGRESS TOWARD MILESTONES

During this quarter we studied the effect of the polymer in the gel electrolyte. The gel is composed of x% polymer-(1-x)%EC-GBL-1.5M LiTFSI. This polymer contains tetrafunctional terminal acryloyl-modified alkylene oxide polymer (four-branch polymer).

Figure 1 shows that the vapor pressure is lower when the amount of GBL is reduced. At high temperature (100-125°C), the vapor pressure decreases when the polymer content increases. This effect helps improve the safety of the battery.

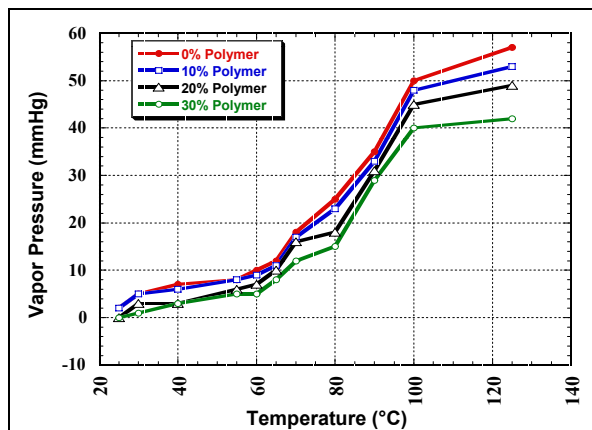


Figure 1: Vapor pressure of the gel polymer as function of temperature.

We have used TGA to investigate the weight loss with different polymer ratios in the gel. The polymer ratios selected were 100%, 30, 20 and 10% by weight. The results in figure 2 show the weight loss as function of polymer content. An increase in the polymer content resulted in a decrease in the weight loss of the gel.

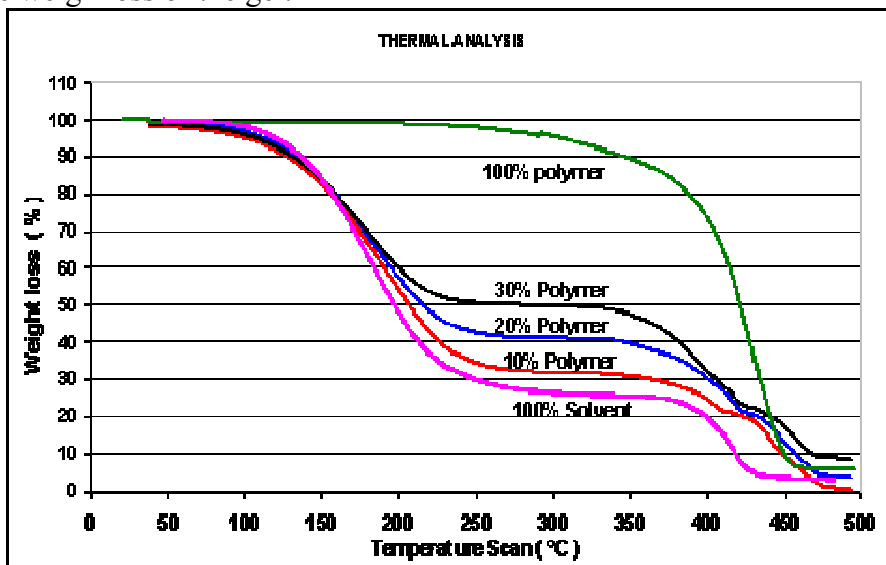


Figure 2: TGA of the gel polymer as function of temperature.

In the second set of experiments, the gel samples were held at a fixed temperature ($T = 60^{\circ}\text{C}$) for 3 hours. After 3 h at 60°C , the weight loss of the different gel compositions (10, 20, 30%W) was comparable (17.3%) within the margin error, independent of the polymer ratio.

Optimization studies of the new HQ gel electrolyte indicated that good mechanical properties are obtained at a 10/90 polymer/liquid weight ratio.

We have evaluated half cells and Li-ion cells with a new low-cost lithium salt, bis(fluorosulfonyl)-LiFSI, developed by the University of Montreal. The results to date indicate stable discharge capacity can be obtained in three-electrode cells.

Another milestone to send cells to LBNL by the end of October 2003 was met. Five (5) cells containing Li-ion gel and LiFSI salt, and with LiFePO_4 cathodes and natural graphite anodes were delivered to LBNL. In addition, 3 extra cells containing LiFePO_4 cathodes and natural graphite anodes, but with LiBF_4 salt were delivered to compare the effect of Li salt on cell performance.

BATT TASK 2

ANODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Anodes - Non-Carbonaceous Materials

SYSTEMS: Low-cost Li-ion

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To replace carbon with an alternative inexpensive anode material that will be compatible, in particular, with low-cost manganese oxide cathodes. The project also addresses the need for improved safety of Li-ion cells.

APPROACH: Our approach has been to search for and develop inexpensive intermetallic electrodes that provide an electrochemical potential a few hundred mV above that of metallic Li, and capacities of 300 mAh/g and ~2000 mAh/ml (the theoretical capacities for graphite are 372 mAh/g and 818 mAh/ml, respectively). The approach will be broadened in FY 2003 to include investigations of standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and electronically-conducting Li-, Mg-, and Al-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes against high-voltage layered and spinel cathodes. Such Li-ion cells, which should be inherently safe compared to conventional Li-ion cells, provide a voltage of ~3 V and may find application in high-power batteries for HEVs.

STATUS OCT. 1, 2002: We have identified several intermetallic compounds that react topotactically with Li, and by reversible Li insertion/metal extrusion processes. The major focus has been placed on $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$, Cu_2Sb and MnSb electrodes. Although these systems operate reversibly within strictly defined voltage limits, they still suffer from an unacceptably large irreversible capacity loss (ICL) on the initial cycle. Oxide surface layers, the choice of electrolyte, and the identity of the binder were determined to have a small effect on lowering the capacity loss, whereas the loss of extruded metal during the initial cycle and electronic isolation were determined to be major contributing factors in the loss of cell capacity. MnSb electrodes showed an ICL of 15-20% (similar to graphite electrodes) compared to $\text{Cu}_{6-x}\text{M}_x\text{Sn}_5$, Cu_2Sb and InSb electrodes (25-40%) and delivered a steady 300 mAh/g for 20 cycles.

EXPECTED STATUS SEPT. 30, 2003: We expect to increase the cycle life of intermetallic electrodes based on tin and antimony to more than 100 cycles with capacities in excess of 300 mAh/g (~2000 mAh/ml) in Li half-cells. We will have completed our initial investigations of standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and Li-, Mg-, and Al-doped $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes that are coupled against high-voltage layered and spinel cathodes.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) a reversible electrochemical capacity of tin- or antimony-based intermetallic electrodes in excess of 300 mAh/g (~2000 mAh/ml) for 100 cycles (September 2003).

(b) 100 cycles from ~3 V cells containing a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -type anode and a high-voltage layered or spinel cathode (September 2003).

PROGRESS TOWARD MILESTONES

Accomplishments

Although our work on antimony-based intermetallic electrodes has shown that we can meet our targeted capacity goal of 300 mAh/g (MnSb and Ag₃Sb systems), the capacity fade after approximately 40-50 cycles and the irreversible capacity loss that occurs during the initial charge/discharge cycle severely limits the cycle life of these types of electrodes (Fig. 1). We are therefore turning our attention to Si- and Sn-based electrodes because, not only do they offer a lower potential compared to Sb-based electrodes, but they are showing greater promise as composite electrodes when combined with graphite. Our preliminary experiments of composite systems such as Si-Sb and Si-C have demonstrated significantly superior electrochemical performance when graphite is used as the medium to act as a buffer for the volume expansion of the metal/Si component (Fig. 2), consistent with reports that are appearing in the literature. Figure 2 shows the excellent cycling stability that was achieved from a Li/Si-2C cell when the capacity of the Si-2C electrode (i.e. in which the Si:graphite ratio = 1:2) was limited to 500 mAh/g during cycling between 0.5 and 0.0 V vs. Li⁰. (This cell failed abruptly at 52 cycles, the reason for which is unknown.) Li/Si-2C cells that were cycled between these voltage limits without imposing a capacity restriction decayed rapidly. Because of the promising data shown in Fig. 2, a major effort will be made during FY2004 to exploit and optimize Si-graphite and metal-graphite composite electrode systems.

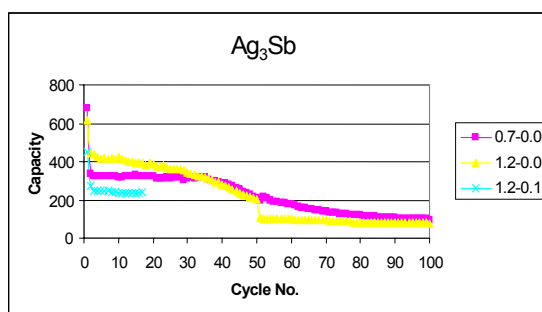


Figure 1. Capacity vs. Cycle No: Li/Ag₃Sb

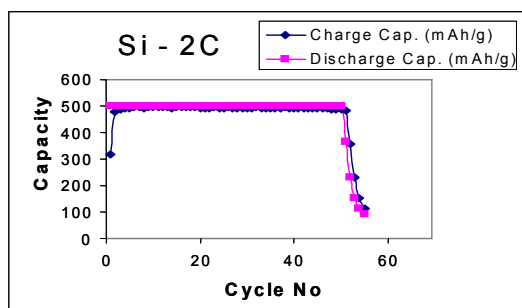


Figure 2. Capacity vs. Cycle No: Li/Si-2C

We are also exploring metal oxides as alternative negative electrodes to graphite. These include the electronically conducting Mg- and Al-substituted Li spinels that are being evaluated against high-potential (>4.5 V) spinel and layered lithium-manganese-nickel-oxide electrodes. This activity complements our work in Cathode Task 4.1; the progress that has been made in exploiting 3.2 V spinel anode/spinel cathode couples has been provided in our cathode report.

We have also initiated a theoretical study of low-potential Li₂MO₂ systems to explore the possibility of using lithiated LiMO₂ compounds, notably lithiated LiVO₂, as insertion electrodes. First principles density-functional-theory calculations with the VASP code are being performed to determine the voltage of such reactions and to predict which of the following possible reactions would be most favorable:

- 1) $\text{Li} + \text{LiMO}_2 \rightarrow \text{Li}_2\text{MO}_2$
- 2) $\text{Li} + \text{LiMO}_2 \rightarrow \text{Li}_2\text{O} + \text{MO}$
- 3) $3\text{Li} + \text{LiMO}_2 \rightarrow 2\text{Li}_2\text{O} + \text{M}$

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Anodes - Novel Materials

SYSTEMS: Low-cost Li-ion battery and gel-electrolyte battery

BARRIER: Cost, safety and volumetric capacity limitations of Li-ion batteries

OBJECTIVES: To replace the presently used carbon anodes with safer materials that will be compatible with manganese oxide cathodes and the associated electrolyte. In particular, we will investigate Mn-tolerant anode materials.

APPROACH: Our anode approach is to explore, synthesize, characterize, and develop inexpensive materials that have a potential about 500 mV above that of pure Li (to minimize the risk of Li plating and thus enhance safety) and have higher volumetric energy densities than carbon. We will place emphasis on simple metal alloys/composites. All materials will be evaluated electrochemically in a variety of cell configurations, and for thermal and kinetic stability.

STATUS OCT. 1, 2002: We have shown that vanadium and manganese oxides, in their highest oxidation states, are not prime candidates. Pure Al was found to have a high capacity and react readily with Li, but its capacity faded rapidly upon cycling in carbonate-based electrolytes; Al-based alloys show behavior inferior to that of pure Al. Tin-containing materials, such as MnSn_2 , cycle well for a few cycles before capacity fade sets in. Pure Sn anodes appear to cycle better than MnSn_2 .

EXPECTED STATUS SEPT. 30, 2003: We expect to have designed a program to understand and remediate capacity fade upon cycling, and as a result to have identified several additional non-Al binary alloys, and to have improved the electrochemical performance of the materials identified.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) We will design a program to identify, understand, and mitigate the capacity loss upon cycling of simple alloy systems. This will result in a milestone to understand the cause of capacity fade in pure tin by June 2003, and to propose a means of remediating that fade. (b) Another major milestone is to identify by September 2003 a new simple material (a binary alloy) that has the potential of higher volumetric capacity than carbon at about 0.5 V relative to pure Li.

PROGRESS TOWARD MILESTONES

In this past quarter we continued our program to understand the cause of capacity fade for tin foil as the anode in lithium batteries. An analysis of our data, shown in Figure 1 (left), shows that after a break-in period the amount of lithium inserted into the tin foil is equal to the amount of lithium removed in the previous half-cycle. This indicates that freshly formed tin is essentially inert in the electrolyte used. Capacity fade must thus be associated with the lithium-tin phase after lithium insertion. Two possible options are: (1) some of the lithium in the tin reacts irreversibly with the electrolyte, thus becoming unavailable for subsequent use, and (2) some of the Li_xSn alloy becomes physically and electronically detached from the electrode so it can no longer participate.

To help determine the impact of the electrolyte salt on the capacity fade, we have also cycled the tin foil in a LiBOB EC/DMC electrolyte cell. The results are shown in Fig. 1 (right). Tin can cycle in this electrolyte; the smaller capacity can probably be associated with the rate used, 1 mA/cm^2 , which is high for this lower-conductivity salt. Our initial studies have also isolated one of the problems associated with LiBOB, its ready reaction with water giving impurities. A crystal structure analysis of LiBOB indicates that it is five coordinate. Thus, it is highly reactive, grabbing almost any polar solvent including water from the atmosphere to gain octahedral 6-coordination. We continue to explore the synthesis and characterization of pure LiBOB, as its use could lead to a fluoride-free environment and it ought to be a lower-cost electrolyte salt.

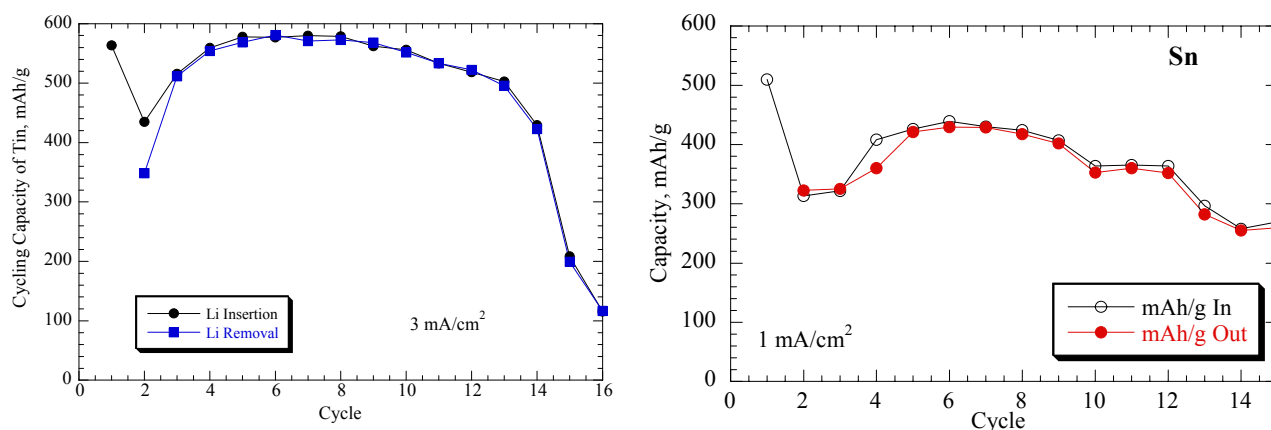


Figure 1. Left): Cycling capacity of tin foil in LiPF_6 , EC/DMC electrolyte, and right) cycling capacity of tin foil in LiBOB, EC/DMC electrolyte.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

1. Shoufeng Yang, Peter Y. Zavalij and M. Stanley Whittingham: "Anodes for Lithium Batteries: Tin Revisited," *Electrochem. Commun.* 2003, **5**: 587-590.
2. Peter Y. Zavalij, Shoufeng Yang and M. Stanley Whittingham: "Structures of potassium, sodium and lithium bis(oxalato)borate salts from powder diffraction data," *Acta. Cryst.* **B59**, in press (2003).
3. Shoufeng Yang, Peter Y. Zavalij and M. Stanley Whittingham: "Anodes for Lithium Batteries: Tin Revisited," presented at Solid State Ionics Meeting, Monterey, California, July 2003 and at Arcachon, France, September 2003.

TASK STATUS REPORT

PI, INSTITUTION: G.A. Nazri and M.D. Curtis, University of Michigan
T. Malinski, Ohio University

TASK TITLE – PROJECT: Anodes - Novel Composite Anode for Lithium-ion Batteries

SYSTEMS: Low-cost Li-ion

BARRIER: Safety, irreversible capacity loss, and self-discharge

OBJECTIVES: Develop a low-cost and safe composite anode plate with no intrinsic irreversible capacity loss (ICL) and with higher gravimetric and volumetric energy density than the current carbonaceous anodes. Improve the kinetics of the Li insertion-extraction process in the composite anodes for application in high-power Li-ion cells.

APPROACH: Prepare composite anodes *via* reactive mechano-milling to eliminate large ICLs of metal-oxide anodes that occur during initial Li charge-discharge cycles. Form a desirable synthetic SEI layer *via* the mechano-reduction of oxide precursors and reduce the anode particle size to nanoscale to improve rate capability.

STATUS OCT. 1, 2002: The optimization of mechano-milling process parameters for reactive reduction of metal oxide anodes was in progress. The chemical nature of the SEI formed on metals and alloys after reduction of their oxide precursors was studied. An electrochemical study of the composite anode in baseline electrolyte (EC-DMC containing 1M LiPF₆) was ongoing. The process of developing composite anodes from mixed metal nitrides and oxides was in progress.

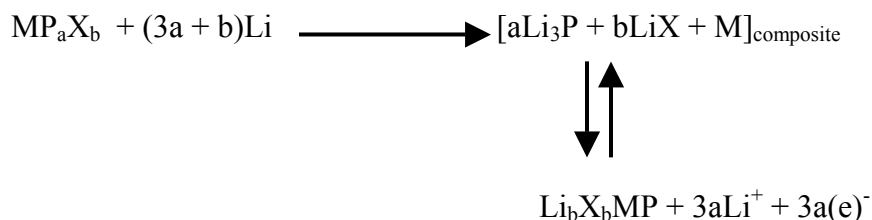
EXPECTED STATUS SEPT. 30, 2003: A well-controlled process based on reactive mechano-milling will be introduced for the preparation of composite anodes from various oxide or nitride precursors. Full characterization of the composite anodes in terms of their chemical composition, particle size, and nature of their SEI layer will be completed. Electrochemical tests of charge-discharge behavior of the composite anodes in terms of voltage profile, reversibility, and overall capacity will be completed. Cycle-life tests of the composite anodes at several levels of active material loading will be continued and accumulated cycle numbers and remaining capacity will be reported.

RELEVANT USABC GOALS: Exceeding 10-year life, low capacity loss (< 20%), good safety and high reliability (no toxic and flammable gas formation).

MILESTONES: (a) Optimization of process parameters for reactive mechano-milling of *sp* metal oxides completed by January 2003. (b) Electrochemical tests including charge-discharge cycle life of composite anodes formed by reactive milling of oxides and nitrides completed by August 2003.

PROGRESS TOWARD MILESTONES

The optimization of prelithiated composite anodes has been completed and reported in previous reports for SnO, SnO₂, PbO, and transition metal oxides CoO, and nitrides and phosphides with emphasis on LiFe₂P. In addition the prelithiation of graphite samples were completed and reported. During the course of this investigation, the safety of lithiated graphite anode was revisited, and we have found that lithiated graphite anode (LiC₆) reacts violently with electrolyte when their surface passivation layers (SEI) are destroyed at slightly elevated temperatures (>120C). Therefore, we have focused on the development of a safer composite anode for application in large-size lithium cells. We have shown in our previous work that composite anodes based on oxides and nitrides may not be practical due to about 1 volt hysteresis overpotential during lithiation and delithiation processes. Based on our success on prelithiation of inorganic compounds such as phosphides, nitrides, oxides and halides, and requirements for high-rate composite anode, we have studied a new transition metal phosphides-halide compound as anode for rechargeable lithium cells. Based on some fundamental considerations, we have focused on mixed phosphides halide of transition metals. The most practical system is based on copper phosphides iodide. The theoretical reversible capacity of the compound is about 665 mAh/g. The first irreversible capacity loss for this compound is less than 20% and this can be eliminated by mechanochemistry during our established prelithiation process. The charge-discharge process for the transition metal phosphohalide is shown according to the following equation.



The M= Cu and X = I. We have selected iodide and phosphides for their better lithium ion conductivity. The active reversible phase is proven to be Li₃P. The transition metal extracted from the compound (in amorphous state) during lithiation process has improved the electronic conductivity of the composite matrix. The presence of LiI also improved the ionic conductivity of the composite matrix.

The irreversible capacity loss of copper phosphohalide is reduced significantly to less than 5% by mechanochemistry. In addition the large hysteresis usually observed for oxides and nitrides are reduced due to the good ionic and electronic conductivity of the composite matrix anode.

Further plans to meet or exceed milestones.

Our future plan is to test the safety aspects and cycle life of the complex composite anodes for large size high power lithium-ion cells.

Reason for changes from original milestones. N/A

BATT TASK 3 ELECTROLYTES

TASK STATUS REPORT

PI, INSTITUTION: N. Balsara, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - Polymers for Li Metal Electrodes and Low-Cost Polymer Gel Cells

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Short Li battery lifetimes, poor ambient-temperature performance for polymer electrolytes, and low energy and power densities due to instability to 4 V.

OBJECTIVES:

- Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth.
- Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop new materials capable of ambient-temperature operation with Li metal.
- Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: To obtain a fundamental understanding of charge transport in polymers through polymer characterization and the synthesis of new materials. Polymers will be characterized by methods such as neutron scattering, dielectric relaxation spectroscopy, and light scattering to obtain new insights into the rate-limiting transport processes.

STATUS OCT. 1, 2002: New investigator.

EXPECTED STATUS SEPT. 30, 2003: The utility of neutron scattering, dielectric relaxation spectroscopy, light scattering, and rheological measurements will be fully explored for dry and gel polymers. A combination of polymer synthesis; physical, chemical, and electrochemical measurements; and theoretical calculations will be used to develop a working hypothesis on the limiting mechanism for Li-ion mobility.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONE: Establish a working hypothesis for the rate-limiting step of Li-ion mobility in polymer electrolytes/polyelectrolytes (09/30/03).

PROGRESS TOWARD MILESTONE

We have synthesized our diblock copolymer system, polyisoprene-b-polyethyleneoxide with polyisoprene being the major phase and the polyethylene oxide chains phase separating into cylindrical channels. The goal is to produce a higher-performance electrolyte by increasing the efficiency of ion transport in the polymer system. We are capable of changing parameters such as the chain length of either block (molecular weight) and the volume fraction of one block relative to the other.

After establishing the synthetic method in our laboratory, we have shown, using Differential Scanning Calorimetry (DSC), that crystallization of the polyethylene oxide chains in our matrix at room temperature is suppressed and stable up to 3 months. This is a major milestone towards our goal because the confinement of the polyethylene oxide chains and lack of crystallization at ambient temperatures will result in better ionic conductivity of our diblock copolymer system.

We have used Small Angle X-ray Scattering (SAXS) to confirm the presence of polyethylene oxide cylinders in our system. The existence of cylinders is a necessary but not sufficient condition to achieving our goals. It is crucial that these cylinders be aligned orthogonal to the electrodes to obtain the enhanced conductivity. We will use electric fields to align these cylinders and Atomic Force Microscopy (AFM) to study the alignment in our system. We have established access to an AFM probe and have developed the competency in imaging the self-assembled features on our samples using the tapping mode.

Spinning our diblock copolymer solutions on piranha-etched silicon wafers and imaging with the AFM has shown that the cylinders are oriented parallel to the surface of the wafer. These AFM studies have revealed a “roadmap” topology, observed by other research groups with different diblock copolymer systems, and further prove the presence of cylinders in our system. We will begin AFM studies on block copolymer/salt mixtures in the near future. Once the desired alignment of the salt-containing cylinders has been accomplished, we will carry out conductivity measurements, using a recently fabricated a home-built conductivity test cell that interfaces with a Solartron Frequency Response Analyzer.

TASK STATUS REPORT

PI, INSTITUTION: J. Kerr, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Electrolytes - R&D for Advanced Lithium Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short Li battery lifetimes, poor ambient temperature performance for polymer electrolytes and low energy and power densities due to instability to 4 V.

OBJECTIVES: Determine the feasibility of the Li metal electrode with organic electrolytes and provide operating conditions that prevent dendrite growth. Determine the limitations on Li-ion transport in polymer electrolytes and composite electrodes and develop materials capable of ambient temperature operation with Li metal. Determine the limits of stability of organic electrolytes at high-voltage cathode materials (*e.g.*, 4 V) and develop materials and methods to increase stability.

APPROACH: A physical organic chemistry approach is taken to electrolyte design, thereby ensuring that not only are the sources of poor performance and failure pinpointed but also the problem can be corrected through materials design and synthesis.

STATUS OCT. 1, 2002: Best polymer electrolyte transport and mechanical properties completed for TMO-containing comb polymers/LiTFSI or LiBETI (85°C: $t_+^0=0.3$, $D_s > 5 \times 10^{-12} \text{ m}^2/\text{s}$, $\sigma = 10^{-3} \text{ S/cm}$; 25°C: $t_+^0=0.2$, $D_s > 10^{-12} \text{ m}^2/\text{s}$, $\sigma \sim 10^{-4} \text{ S/cm}$, $E_g(\text{compression}) > 10^6 \text{ Pa}$). Less-costly salts (LiTf, LiPF₆ and LiBF₄) will also be measured and the cost vs. performance will be assessed. Dendrite-free cycling for > 500 coulombs in full cells at 0.2 mA/cm² [Lab cell (4cm²)]. Lithium/polymer cell testing at a larger cell size (*e.g.*, 12.5 or 25cm² area) will be established

EXPECTED STATUS SEPT. 30, 2003: Effects of filler particles and cross-linking on transport and mechanical properties will be quantified for polymer electrolytes, polyelectrolytes, and polymer gels. Full and half-cell cycling and calendar tests will be used to quantify chemical side reactions and physical changes that limit battery life.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade over a 10-year period, 1000 cycles, operating environment -40 to 65°C, specific energy >170 Wh/kg, specific power >300 W/kg, <150\$/kWh @ 20K/year.

MILESTONE: Demonstrate dendrite-free cycling of Li metal electrodes in full cells (Li/V₆O₁₃) and half-cells (Li/Li) for >1000 coulombs of charge (USABC goal >8,000 coulombs) at >0.5 mA/cm² with cell polarizations of <200mV(full cell) and <50mV(half-cell) at ≤60°C (09/30/03).

PROGRESS TOWARD MILESTONE.

1) No binary salt electrolyte containing ethylene oxide (EO) solvation units (*e.g.*, PEO) have been found with sufficiently high salt diffusion coefficients at 60°C to meet the cell polarization requirements at the specified current densities. Typical values at 60°C are 2-3 x 10⁻⁸ cm²/s for linear PEMO-LiTFSI or comb-branch PEPE_x-LiTFSI. There is a large increase in D_s upon raising the temperature to 85°C (6 x 10⁻⁸ cm²/s for both). *These electrolytes are able to sustain the specified current densities at 85°C but do not inhibit dendrite growth at this temperature without some form of mechanical strengthening.*

2) Linear polymers containing trimethylene oxide (TMO) solvation units, i.e. $\text{--O--CH}_2\text{CH}_2\text{CH}_2\text{--O--}$, have much higher salt diffusion coefficients, $6 \times 10^{-8} \text{ cm}^2/\text{s}$ at 60°C and $1.2 \times 10^{-7} \text{ cm}^2/\text{s}$ at 85°C and can sustain the specified current densities. *We have not yet prepared a cross-linkable form of linear TMO polymers that has the required mechanical properties.*

3) Comb-branch polymer electrolytes containing TMO units in the side chains but PPO or polyacrylate backbones have lower D_s values than the linear TMO polymers at higher temperatures (60° and 85°C) and higher D_s values at low temperatures (25°C). These materials can be cross-linked to give the required mechanical properties but cannot sustain the desired current densities. The propylene oxide and acrylate units in the backbones act as traps for the lithium ions and slow the diffusion rates. *A new backbone is required in order to achieve the full benefits of the TMO solvation units in this architecture.*

4) *We have found that polymer electrolytes require an elastic shear modulus of at least 10^6 Pa and a Poisson Ratio of 0.5 to inhibit dendrite growth.* Such properties may be obtained by cross-linking the polymer and by addition of nano-particle fillers. Cross-linking may be achieved by covalent bonds or by ionic means due to the presence of lithium salts. The transport properties of the lithium salts are reduced by the addition of fillers that interact strongly with the polymers and also by dense cross-linking. Since the transport properties of the unmodified polymer electrolytes barely meet the requirements, the addition of fillers and cross-linking can impair the transport to the point where severe concentration polarization occurs. We have found that fillers with modified surfaces and comb-branch polymer architectures with appropriate cross-linking can provide the desired mechanical strength without severe impact on the transport properties. *It is also noted that the ionic cross-links in TMO polymers are considerably weaker than in EO polymers so that these polymers are less affected by concentration gradients.*

5) *Rheological measurements have shown that the mobility of polymer electrolytes is inhibited by the presence of surfaces, including electrode surfaces.* We have observed the occurrence of transition times in lithium/lithium cycling experiments at current densities well below the calculated limiting current. During lithium-lithium cycling experiments with cross-linked polyacrylate ethers the apparent salt diffusion coefficients of LiTFSI were estimated from the relaxation curves after polarization for 2 coulombs of charge passed at $200 \mu\text{A}/\text{cm}^2$ at 85°C . The salt diffusion coefficient decreased by 15% after only 5 cycles. Similar estimates were carried out for composite cathodes (V_6O_{13}) by observing the relaxation of the cathode potential versus a lithium reference electrode at the end of discharge. The apparent salt diffusion coefficient decreased by 50% after eleven cycles. *These effects appear to be caused by salt concentration gradients that induce phase changes in the polymers at the electrode surfaces and severely restrict ionic mobility.*

6) The interfacial impedance of polymer electrolytes at electrodes increases rapidly as the temperature is decreased. With Li/Li cells, PEO-LiTFSI has the following interfacial impedances: 85°C , $50 \Omega\text{cm}^2$; 60°C , $300 \Omega\text{cm}^2$; 40°C , $3000 \Omega\text{cm}^2$. Similar trends are observed with PEGDME250 and PEGDME500-LiTFSI but the magnitude of the interfacial impedance is ten times lower. These effects can be rationalized by the interaction of the electrolytes with the electrode surfaces. The high interfacial impedance of high molecular weight polymers at lower temperatures significantly increases the cell polarization to untenable levels. The interfacial impedances may be altered by modifications of the lithium and cathode surfaces.

Conclusion. *It is likely that dendrite suppression at lithium metal electrodes can only be achieved for interesting current densities through the use of single-ion conductor electrolytes that remove concentration polarization, are mechanically strong and do not exhibit high interfacial impedances at electrodes.*

TASK STATUS REPORT

PI, INSTITUTION: S.A. Khan, P.S. Fedkiw, North Carolina State University;
G.L. Baker, Michigan State University

TASK TITLE - PROJECT: Electrolytes - Composite Polymer Electrolytes for Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer

BARRIER: Short lithium battery lifetimes and high costs

OBJECTIVES: The ultimate objectives are to develop composite polymer electrolytes that are low-cost, have high conductivities, impart electrode-electrolyte interfacial stability, and yield long cycle life.

APPROACH: Our approach is to use surface-functionalized fumed silica fillers in BATT-baseline and candidate systems to determine the effects of filler type and concentration on interfacial stability and cell cycling. We correlate these electrochemical characteristics with mechanical properties and materials chemistry (*e.g.*, silica-type or PEO-type, synthesized by Baker or Kerr, respectively). Data collected include elastic and viscous moduli, ionic conductivity, transference number, Li cycling efficiency, Li-electrolyte interfacial resistance, and full-cell cycling capacity using 3-V cathodes.

STATUS OCT. 1, 2002: We have established that fumed silica-based composite electrolytes with low-molecular weight (MW) PEOs exhibit conductivities exceeding 10^{-3} S/cm at 25°C and have electrochemical properties decoupled from mechanical properties. We have determined that fumed silica stabilizes the Li/electrolyte interface, and effectively suppresses Li dendrite growth. We have found that addition of fumed silicas into low-molecular weight PEOs significantly improves charge-discharge cycle performance, coulombic and energy efficiencies, rate capabilities, and self-discharge performance of Li/V₆O₁₃ cells. We have determined that adding fumed silica improves the rheological properties of high-MW polymer electrolytes, but can be either beneficial or detrimental to ion-transport behavior. We have also found that adding fumed silica improves the interfacial stability of Li/electrolyte (high-MW PEO) interface and cycle performance of Li/V₆O₁₃ cells.

EXPECTED STATUS SEPT. 30, 2003: Using mixed-MW (high- + low-MW) PEOs + LiTFSI as the base electrolyte, we expect to determine the effect of fumed silica on conductivity and electrolyte/Li interfacial stability and how these results vary with type of fumed silica surface group.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) Interfacial stability and full-cell cycle studies of mixed polymer system completed by September 2003. (b) Rheological data for mixed-MW polymer system acquired for correlation with electrochemical stability by September 2003.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestones over last quarter:

We have dynamic rheological results of mixed-MW polymer electrolytes, P(EO)₂₀LiTFSI (PEO (600K):PEG-dM (250)=1:1 (mass); Li:O=1:20), which were measured over a temperature range of 80 to 25 °C. The addition of fumed silica to the electrolyte changes its rheological response under shear in that the material becomes more elastic and less frequency dependent for all temperatures evaluated. These trends indicate the reinforcing effect of the nanoparticles, even at high temperatures where the polymer is in the melt state and no crystalline structure is present. The conductivity increases considerably in the same temperature range where a decrease in the elastic modulus (G') is observed. Melting and glass transition temperatures of mixed-MW electrolytes will be evaluated using differential scanning calorimetry by the next report. These results will be correlated with the observed change in conductivity and rheology.

We have collected half-cell and full-cell cycling results at 65°C for mixed-MW polymer electrolytes P(EO)₂₀LiTFSI (PEO(600K) + PEG-dM(250) + LiTFSI (Li:O=1:20)). Li/CPE/Li cells were cycled at a current density of 1 mA/cm² with a charge density of 240 mC/cm². The cell voltage increases considerably for electrolyte without fumed silica, whereas the cell voltage is more stable for electrolyte containing fumed silica. This result suggests that adding fumed silica into mixed-MW polymer electrolyte attenuates lithium dendrite formation and improves the lithium/electrolyte interfacial stability. These effects have also been demonstrated for full-cell cycling of Li/electrolyte/V₆O₁₃, with the vanadium oxide cathodes consisting of 40 wt% V₆O₁₃ (Kerr-McGee), 7.5 wt% graphite (Timcal American), 2.5 wt% Ketjen-Black600 (Akzo Nobel), and 50 wt% (PEO)₂₀LiTFSI. In the full-cell Li/electrolyte/V₆O₁₃ system, cycle performance improves with addition of fumed silica when cycling at 0.05 mA/cm² from 1.7 to 3.1 V. Investigations with cathode tunnel compound MnO₂ (supplied by BATT investigator Dr. Doeff) will begin when the material is made available to our group.

We have studied the effect of fumed silica on aluminum corrosion using low-MW PEO electrolyte (PEG-dM (250) + LiTFSI; Li:O=1:20). Li/electrolyte/Al cells and two types of Al foil (one from Fisher and the other from Celgard) were employed at room temperature. The open-circuit voltage for cells with fumed silica-based gel electrolytes was more stable than that for baseline liquid electrolyte; the current density for gel electrolytes was lower and changed less with increasing potential in LSV measurements than that for baseline liquid electrolyte; and the impedance for gel electrolytes was more stable than that for baseline liquid electrolyte. Gel electrolytes have higher pitting resistance than baseline liquid electrolyte according to an equivalent-circuit analysis of the data. Three possible reasons may explain the enhanced aluminum corrosion resistance affected by fumed silica: covering a defect site in the oxide film, scavenging moisture from the electrolyte, and increasing adhesion of salt films on the aluminum surface. A manuscript discussing these results is under preparation for submission to *Electrochemical & Solid State Letters*.

Further plans to meet or exceed milestones: We will vary the composition and concentration of the blends in an attempt to improve both conductivity and mechanical properties. We are setting up a heating system on a microscope stage to study dendrite formation at elevated temperature ($T \approx 65^\circ\text{C}$) using the mixed-MW polymer electrolytes. We will also begin collaboration with BATT investigators Drs. DesMarteau and Creager to test their new imide salts and single-ion conductors.

Reason for changes from original milestone: N/A

TASK STATUS REPORT

PIs, INSTITUTION: D. DesMarteau and S. Creager, Clemson University

TASK TITLE - PROJECT: Electrolytes - New Battery Electrolytes based on Oligomeric Lithium bis((perfluoroalkyl)sulfonyl)imide Salts

SYSTEMS: Li/polymer

BARRIER: Poor electrolyte transport properties, low power density, short lifetime

OBJECTIVES: (1) Develop methods for synthesizing oligomeric ionene Li salts based on the bis((perfluoroalkyl)-sulfonyl)imide anion. (2) Develop methods for preparing solid polymer electrolytes (SPEs) from the target salts. (3) Provide data on transport properties, especially ionic conductivity and Li ion transference, for target SPEs at variable temperature and composition.

APPROACH: Salts will be synthesized using methodologies developed at Clemson over the last 15 years (D. DesMarteau, *J. Fluorine Chem.* 1995, **72**, 203-208). SPEs will be prepared from crosslinked low-MW polyethylene glycol (PEG) and also non-crosslinked PEG for comparison. Transport properties will be measured using electrochemical impedance spectroscopy combined with other electrochemical techniques including restricted diffusion, DC polarization, and concentration cell techniques.

STATUS OCT. 1, 2002: A series of dimeric Li salts with different perfluorinated chains linking sulfonyl imide anions together, and selected oligomeric ionene salts utilizing perfluoroalkyl linkers in longer chains, were synthesized. SPEs from the salts will be fabricated in polyether matrices, and their ionic conductivities measured at various temperatures and compositions.

EXPECTED STATUS SEPT. 30, 2003: Synthetic methods will be refined for tetra-anionic imide Li salts with a range of different perfluoroalkylene chains linking imide groups, and for oligomeric imides. Ionic conductivities will be measured for SPEs made using all new salts. For salts that exhibit especially favorable behavior a more complete set of transport data including transference and salt diffusion measurements will be made, initially in collaboration with other BATT Program participants and later at Clemson. Salts that exhibit especially favorable properties will also be synthesized in larger quantities and made available to other BATT Program participants for further testing.

RELEVANT USABC GOALS: 10 year life, <20% capacity fade, specific power 300 W/kg.

MILESTONES: (a) Prepare oligomeric Li salts of the type $\text{CF}_3\text{SO}_2[\text{N}(\text{Li})\text{SO}_2\text{R}_f\text{SO}_2]_n\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ with variable fluorocarbon linkers and systematic variation of the average n values. Refine synthetic methodology to improve yields, purity, and ease of the multi-step syntheses. (b) Perform a full transport properties study including measurement of conductivity and Li transference across a range of salt concentrations for a representative oligomeric imide salt. Milestones to be completed by September 2003.

PROGRESS TOWARD MILESTONES

All members of the ionene series of structure $\text{CF}_3\text{SO}_2\text{N}(\text{Li})[\text{SO}_2(\text{CF}_2)_x\text{SO}_2\text{N}(\text{Li})]_n\text{SO}_2\text{CF}_3$ with $x=4,6$ and $n=0,1,3,5$, and 17 have now been synthesized. Synthetic methods have been refined; in particular a step-growth polymerization scheme was developed to enable preparation of ionenes of systematically variable length in pure form. This activity completes the first milestone for the 10/02 - 9/03 period. Each new salt has been used to prepare solid-polymer electrolytes using high-molecular-weight PEO as host. A complete study focusing on salt structure effects on ionic conductivity has been completed and is described in two manuscripts, one which recently appeared and one which is in review. A study using restricted diffusion techniques to measure salt diffusion coefficients for a series of ionenes with $n = 0,1,3,5,17$, and 225 was completed in this report period. A manuscript describing preliminary results has been submitted for a proceedings volume, and a more comprehensive manuscript is in preparation. Samples have also been supplied to Steve Greenbaum at CUNY for measurement of anion and cation diffusion coefficients by PFG-NMR, which will complement salt diffusion measurements made at Clemson.

Table I. Salt diffusion coefficients and ionic conductivities for PEO-based SPEs prepared using ionene salts of structure $\text{CF}_3\text{SO}_2\text{N}(\text{Li})[\text{SO}_2(\text{CF}_2)_x\text{SO}_2\text{N}(\text{Li})]_n\text{SO}_2\text{CF}_3$ with $x=4$ and $n=0,1,3,5$, 17, and 225. EO/Li = 30/1, $T = 90^\circ\text{C}$.

Salt Type	$(D_s \pm \sigma) \cdot 10^{-8}$ (cm^2/sec)	$\kappa \cdot 10^{-3}$ (S/cm)	Li Salt Conc. (wt%)
$n = 0$ (LiTFSI)	4.2 ± 0.8	1.33	17.9
$n = 1$	1.9 ± 0.7	0.20	19.4
$n = 3$	1.6 ± 0.3	0.24	20.2
$n = 5$	1.3 ± 0.3	0.34	20.5
$n = 17$	0.5 ± 0.06	0.58	20.8
$n = 225$	0.4 ± 0.08	0.04	20.8

Initial transference number estimates have been made using impedance techniques, and more rigorous measurements are in progress using combined impedance / galvanostatic polarization / restricted diffusion / concentration cell measurements. This will complete the second milestone for the 10/02 - 9/03 period.

Recent work at Clemson has focused on synthesis of allyl ether salts for use in making single-ion conductors from allyl-ether-modified polyethers using hydrosilyl coupling chemistry. Salts of structure $\text{CH}_2=\text{CHCH}_2\text{O}-\text{CF}_2\text{CFHO}-\text{CF}_2\text{CF}_2-\text{X}$, with $\text{X}=\text{SO}_3(\text{Li})$ (sulfonate) and $\text{X}=\text{SO}_2\text{N}(\text{Li})\text{SO}_2\text{CF}_3$ (imide) have been synthesized. Approximately 5 g quantities of each salt were shipped to John Kerr at LBNL in mid-October. Work is in progress aimed at synthesizing large (approx. 25 g) quantities of salts of structure $\text{CF}_3\text{SO}_2\text{N}(\text{Li})[\text{SO}_2(\text{CF}_2)_x\text{SO}_2\text{N}(\text{Li})]_n\text{SO}_2\text{CF}_3$, $x=4$ and $n=3$ and 17, for use by other BATT workers in tests with composite silica-based electrolytes, half-cell and full-cell cycling experiments, and aluminum corrosion experiments. Finally, work has begun at Clemson aimed at using allyl ether salts similar to those described above, and related ionene allyl ether salts, to prepare novel polyether-based ionic liquids which should have high conductivity and behave as single-ion conductors.

TASK STATUS REPORT

PI, INSTITUTION: G.D. Smith and O. Borodin, University of Utah

TASK TITLE - PROJECT: Electrolytes - A Molecular Dynamics Simulation Study of the Influence of Polymer Structure on Complexation Thermodynamics, Kinetics and Transport of Lithium Cations in Polyether-based Solid Polymer Electrolytes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Poor cation transport properties in solid polymer electrolytes

OBJECTIVES: Study the influence of polymer structure on ion complexation, dynamics and transport properties of polyether-based polymer electrolytes. Estimate the success of various strategies for the design of solid polymer electrolytes with improved transport properties.

APPROACH: Employ ab initio quantum-chemistry calculations to obtain energetics of polyether complexes with Li-salts and use these data to develop classical force fields for polyether/LiBF₄. Extend these studies to single-ion conductors and gel electrolytes. Use atomistic molecular dynamics simulations of polyether-based Li polymer electrolytes for parametric investigation of the influence of polyether structure, strength of the polyether-Li and Li-anion interactions and barrier of conformational isomerization reaction on ion transport.

STATUS OCT. 1, 2002: Force fields for poly(ethylene oxide)/LiBF₄, poly(oxymethylene)/LiBF₄, poly(propylene oxide)/LiBF₄, and poly(trimethylene oxide)/LiBF₄ were developed. Molecular dynamics simulations of these linear polyethers were performed.

EXPECTED STATUS SEPT. 30, 2003: A force field for the poly(ethylene oxide-trimethylene oxide) (EO-TMO) alternating copolymer doped with LiBF₄ will be developed. Molecular dynamics simulations of linear polyether-based polymer electrolytes will be completed, including EO-TMO. Parametric studies of the influence of PEO-Li⁺ interaction of structural and dynamic properties will be completed. A force field for comb-branch copolymers with polyether side chains will be developed and validated. The mechanism of ion transport in comb-branch copolymers with polyether side chains will be determined. Molecular modeling of gel electrolytes and single ion conductors will be initiated. MD simulations will be performed on liquid electrolytes (EC/LiTFSI) and initiated for comb-branched PEO based gels with EC plasticizer and TFSI⁻ anion attached to side-chains.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade.

MILESTONES: (a) Complete studies of linear polyether-based polymer electrolytes doped with LiBF₄ and parametric studies of the influence of PEO-Li⁺ interaction of structural and dynamic properties (February 2003)
(b) Develop quantum chemistry based force field for ethers/LiTFSI perform analysis of ion transport in comb-branch copolymers with polyether side chains (July 2003)
(c) Initiate MD simulations of PEO-based single ion conductors and gel electrolytes (September 30, 2003).

PROGRESS TOWARD MILESTONES

MD simulations of linear PEO($M_w=2380$)/LiTFSI, Li:ether oxygen (EO) ratio of 15:1 at 393 K have been performed in order to validate the ability of the previously developed quantum chemistry based force field to predict the Li^+ cation environment, anion and cation self-diffusion coefficients and conductivity in this widely investigated polymer electrolyte. The Li^+ cation environment was consistent with the results of the neutron scattering with isotopic substitution experiments performed at EO:Li=1:7.5 ratio (Mao et al., *Phys. Rev. Lett.*, 84, 5536, 2000). The ion self-diffusion coefficients from MD simulations are compared with the results of pulsed magnetic field gradient NMR experiments in Fig. 1. MD simulations predictions are within 25% of the experimental results, indicating that our quantum chemistry based force field is able to accurately capture the $\text{Li}^+/\text{TFSI}^-$ and Li^+/PEO interactions. Similar quality agreement is obtained for conductivity.

Next, we extended the PEO/ $\text{Li}^+/\text{TFSI}^-$ force field to be able to describe the relative conformational energies and barriers between most stable conformers for the side group termination of the single-ion conductor shown in Fig. 2. Development of a set of nonbonded parameters for this polymer and its interactions with the Li^+ cation has been completed.

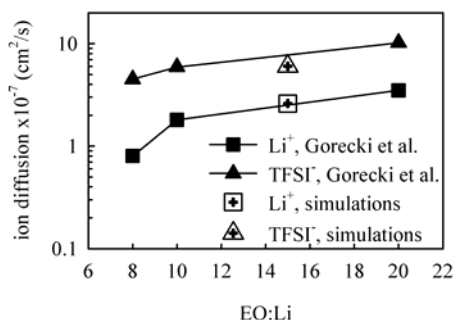


Figure 1. The Li^+ and TFSI^- ion self-diffusion coefficients from MD simulations and experiments (Gorecki et al., *J. Phys.: Condens. Matter*, 7, 6823, 1997).

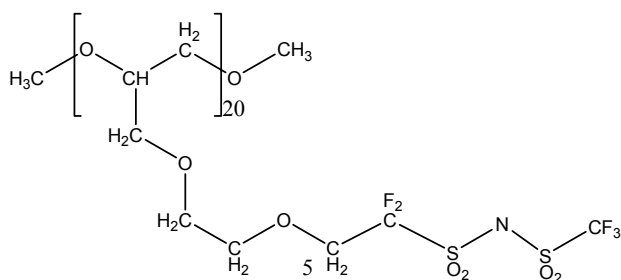


Figure 2. Polymer chain used in simulations of single-ion conductor and gel electrolytes.

MD simulations have been performed on single ion conductor and gel electrolytes. The polymer shown in Fig 2, similar to the PEPE5 comb-branch polymer used by John Kerr's group, was used as a matrix. The Li^+ cations and EC molecules at the ratio of EC:Li=4:1 at 363 K have been added to the polymer matrix (Fig. 2) to create gel electrolyte. The fraction of "free" Li^+ cations in the gel electrolyte was about 70%. Each Li^+ cation was complexed, on average, by approximately 1.8 EC molecules, 1.8 ether oxygen groups and 0.4 oxygen atoms from the TFSI^- anion. MD simulation results indicate that the PEO-based polymer matrix is involved in Li^+ complexation and transport. Because of complexation of the TFSI^- baring end groups and PEO-side chains, the Li^+ self-diffusion coefficient is approximately two times slower than that of the ethylene carbonate molecules. We found that the conductivity of the gel electrolyte was 8×10^{-3} S/cm, which is sufficiently high for use in electric vehicles, and is consistent with the results of Xiaoguang Sun from John Kerr's group for the PEO-based gel electrolytes with sulfonate groups and ethylene carbonate/propylene carbonate plasticizer presented at the 2003 review meeting.

Reasons for changes from original milestones: N/A

BATT TASK 4 CATHODES

TASK STATUS REPORT

PI, INSTITUTION: M. Thackeray, Argonne National Laboratory

TASK TITLE: Cathodes - Novel Materials

SYSTEMS: Low-cost (Li-ion) battery

BARRIER: Cost and safety limitations of Li-ion batteries

OBJECTIVES: To develop low-cost manganese oxide cathodes to replace LiCoO₂.

APPROACH: Our approach is to search for, characterize, and develop low-cost manganese oxide electrodes for Li-ion cells. We will continue to focus on composite layered lithium-manganese oxide structures that are represented by the general formula $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ in which $\text{M}' = \text{Mn, Ti, Zr, Ru}$ and $\text{M} = \text{Li, Mn, Ni, Co}$ are showing excellent promise to replace LiCoO₂ as the cathode material of choice in Li-ion cells. In conjunction with our anode project, we will explore the electrochemical properties of high-potential layered and spinel electrodes against Li₄Ti₅O₁₂ and substituted, electronically-conducting Li₄Ti₅O₁₂ anodes in 3 V Li-ion cells that should be inherently safe.

STATUS OCT. 1, 2002: Preliminary investigations of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrodes in which a Li₂M'O₃ component ($\text{M} = \text{Mn, Ti, Zr}$) was used to stabilize layered LiMO₂ electrode structures, particularly LiMn_{0.5}Ni_{0.5}O₂, were undertaken. These electrodes tend to show a relatively large irreversible capacity loss (ICL) during the initial cycles, but thereafter cycle with good electrochemical reversibility, and provide a rechargeable capacity of approximately 140 mAh/g between 4.6 and 2.5 V at room temperature and 160-170 mAh/g at 50 °C. These electrodes can accommodate extra Li to form Li₂MO₂ compounds with remarkable reversibility and without destroying the integrity of the layered structure; this finding has implications for using the surplus Li in Li₂MO₂ structures to combat the ICL at graphite and intermetallic negative electrodes.

EXPECTED STATUS SEPT. 30, 2003: Improvements in the electrochemical performance of $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes will have been achieved; the targeted performance goal is 190 mAh/g for 100 cycles at 50°C in Li-ion cells. The feasibility of using overdischarged electrodes (with Li₂MO₂ structures) as a reservoir for Li to combat ICL effects in Li-ion cells will have been determined. Composite $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ electrodes and spinel electrodes will have been evaluated against Li₄Ti₅O₁₂ and substituted Li₄Ti₅O₁₂ electrodes in ~3 V cells.

RELEVANT USABC GOALS: 10-year life, <20% fade over a 10-year period.

MILESTONES: (a) Evaluate $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrodes against a technical target of 190 mAh/g for 100 cycles at 50°C, and determine the feasibility of using overdischarged electrodes as a reservoir for Li; and (b) evaluate the electrochemical properties of composite $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ and spinel electrodes against modified Li₄Ti₅O₁₂ electrodes. (September 2003)

PROGRESS TOWARD MILESTONES

Accomplishments

During the past contract period, we continued our efforts to stabilize $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMO}_2$ composite electrode structures in an attempt to reach our targeted capacity of 190 mAh/g at 50°C from $x\text{Li}_2\text{M}'\text{O}_3 \bullet (1-x)\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ electrode systems ($\text{M}'=\text{Ti, Zr, Mn}$). We have almost reached this goal from a $\text{Li}/0.03\text{Li}_2\text{MnO}_3 \bullet 0.97\text{LiMn}_{0.5}\text{Ni}_{0.5}\text{O}_2$ cell, the cathode delivering 175 mAh/g at 50°C between cycles 50 and 100. The first 50 cycles were conducted at room temperature but they yielded a cathode capacity of 145 mAh/g, which is considerably less than the targeted (50°C) goal. Because of the promise that lithium-manganese-nickel oxides hold, we will continue our efforts in FY2004 to increase the room-temperature capacity and to reduce the irreversible capacity loss that occurs when cells are initially charged above 4.3 V. By lowering the voltage of these cells to 1.45 V to access a Li_2MO_2 -type structure, electrode capacities well in excess of 200 mAh/g have been achieved. The high reactivity and structural instability of $\text{Li}_2\text{Mn}_{0.5}\text{Ni}_{0.5}\text{O}_2$, when exposed to air, compromises the possible use of chemically prepared “overdischarged” Li_2MO_2 electrodes for offsetting the irreversible capacity loss that occurs at the negative electrodes of lithium cells.

In response to our stated goals and milestones for FY2003, we initiated studies of 4.7 V- spinel cathodes against 1.5 V Mg- and Al-substituted $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (electronically conducting) anodes which, when coupled together, provide 3.2 V cells. This project is complementary to the goals set in our Anode Task 2.1. These studies are being undertaken against the more stable 2.5 V $\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{Al-substituted})/\text{Li}_{1+x}\text{Mn}_{2-x}\text{Al}_x\text{O}_4$ system as a reference. Figure 1 shows the capacity vs. cycle number plots for a 3.2 V $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{Al-substituted})/\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cell and a 2.5 V $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{Mg-substituted})/\text{LiMn}_{1.975}\text{Al}_{0.025}\text{O}_4$ cell. Although both 3.2 V and 2.5 V cells show excellent cycling stability after the first cycle, the irreversible capacity loss on the first cycle of the 3.2 V cell is significantly worse than it is for the 2.5 V cell. This finding is consistent with the electrochemical behavior of the layered lithium-manganese-nickel-oxide composite electrodes, described above, if charged above 4.3 V (vs. Li^0). This irreversible capacity loss is attributed to the removal of electrons from the oxygen 2p band, and a concomitant loss of oxygen, either as a gas or by reaction with the electrolyte. We are therefore following a similar approach to stabilize the surface of both high-potential layered and spinel lithium-manganese-nickel-oxide cathodes by applying protective coatings and by introducing scavengers of H_2O and HF to minimize the initial capacity loss of these electrodes.

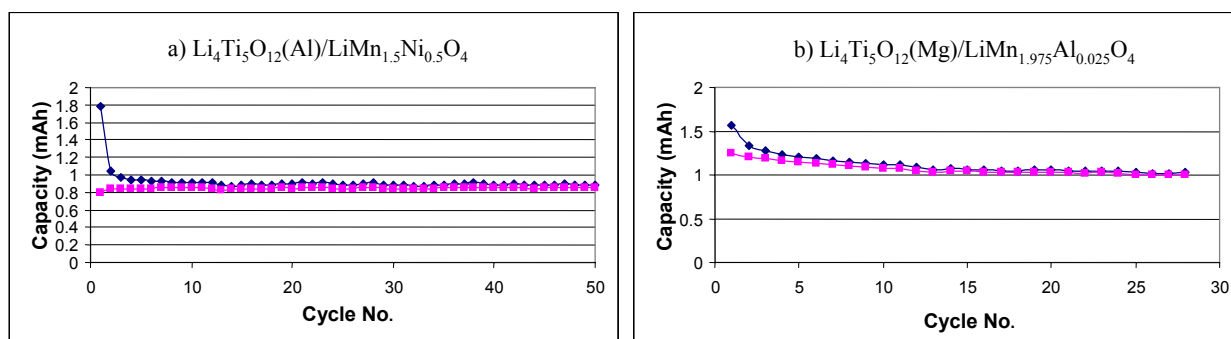


Figure 1. Cell capacity vs. cycle no. plots for a) 3.2 V $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{Al-substituted})/\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ and b) 2.5 V $\text{Li}/\text{Li}_4\text{Ti}_5\text{O}_{12}(\text{Mg-substituted})/\text{LiMn}_{1.975}\text{Al}_{0.025}\text{O}_4$ cells (top curve=charge capacity; lower curve=discharge capacity).

TASK STATUS REPORT

PI, INSTITUTION: M.S. Whittingham, SUNY at Binghamton

TASK TITLE - PROJECT: Cathodes – Novel Materials

SYSTEMS: Li/polymer/gel and low-cost Li-ion

BARRIER: Lower-cost, higher-capacity and safer cathodes

OBJECTIVES: The primary objective is to find lower-cost and higher-capacity cathodes, exceeding 200 Ah/kg, that are based on benign materials.

APPROACH: Our cathode approach is to place emphasis on manganese dioxides, both pure and modified with other transition metals, using predominantly low-temperature synthesis approaches. These materials will be synthesized and characterized, both structurally and for thermal and chemical stability. All will be evaluated electrochemically in a variety of cell configurations.

STATUS OCT. 1, 2002: We have determined that layered manganese dioxides can be structurally stabilized, and that their electronic conductivity and cycling can be significantly enhanced by the addition of other transition metals. We will show the effectiveness of conductive coatings for enhancement of capacity. We will have completed an evaluation of LiFePO_4 as a base-case low cost cathode, and have shown that hydrothermal synthesis is not a viable approach. We will also have shown that vanadium oxides can also be stabilized by the addition of manganese ions to attain capacities greater than 200 mAh/g. In summary:

- LiFePO_4 : > 120 mAh/g for 100 cycles at 1 mA/cm².
- Layered $\text{Li}_x\text{Co}_z\text{Ni}_y\text{Mn}_{1-y-z}\text{O}_2$: 180-200 mAh/g for 5 cycles
- Layered $\text{A}_z\text{Mn}_{0.1}\text{V}_2\text{O}_5$ (A= NH_4 or TMA): ≥ 200 mAh/g for 6 cycles.

EXPECTED STATUS SEPT. 30, 2003: For low-cost Li-ion cells, we expect to identify the changes in stabilized LiMnO_2 structures as a function of current density and substitution level in $\text{Li}_x\text{Mn}_{1-y-z}\text{Ni}_y\text{Co}_z\text{O}_2$, to determine the optimum substitution level and the role of cobalt, to determine the structure and composition of the vanadium stabilized LiMnO_2 and to increase its electrochemical capacity. For Li/polymer cells we expect to complete the evaluation of the manganese stabilized δ -vanadium oxides and to compare them to the iron phosphates. We will also have evaluated possible variants on iron phosphate as base case cathodes. Emphasis in all cases will be placed on understanding the reasons for capacity fade.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) To characterize the stabilized (geometrically and electronically) manganese oxide, determine the optimum substitution of Mn to obtain a capacity of 200 mAh/g, and to compare the best samples with iron phosphates. (b) To complete the characterization of manganese-stabilized vanadium oxides by June 2003 and to compare the best samples with lithium-iron and other phosphates for use in polymer or gel batteries.

PROGRESS TOWARD MILESTONES

(a) Electronic Stabilization of Manganese oxide. This Quarter we continued the characterization of our preferred 442 composition $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$, which we showed earlier to have optimum behavior. These compounds show very little polarization on cycling. However, the temperature of synthesis has a marked impact on the capacity loss on the first cycle and on the subsequent cycling capacity. Thus, all our work is restricted to compounds made between 800 and 900°C. We find that this compound, even without any special conductive coatings, supports a higher capacity at all discharge rates than carbon-coated LiFePO_4 . These data are shown in Fig. 1(left). We expect, as shown by us earlier, that carbon coatings formed *in situ* from carbon gels will have a positive impact on the rate capability of these layered nickelates (BATT 1Q2002). We will explore the impact of such coatings on this 442 composition.

We have characterized the compounds formed as lithium is removed from the 442 composition. These materials appear to be single phase by x-ray analysis from $x=1$ to very low x -values, $x \leq 0.1$, where there some evidence appears for the formation of a second phase. The lattice parameters as a function of lithium content are shown in Figure 1 (right). The a axis increase is consistent with the increased electron density on the oxygen. The volume increases by just 4 % as the lithium content increases from 0.05 to 1.

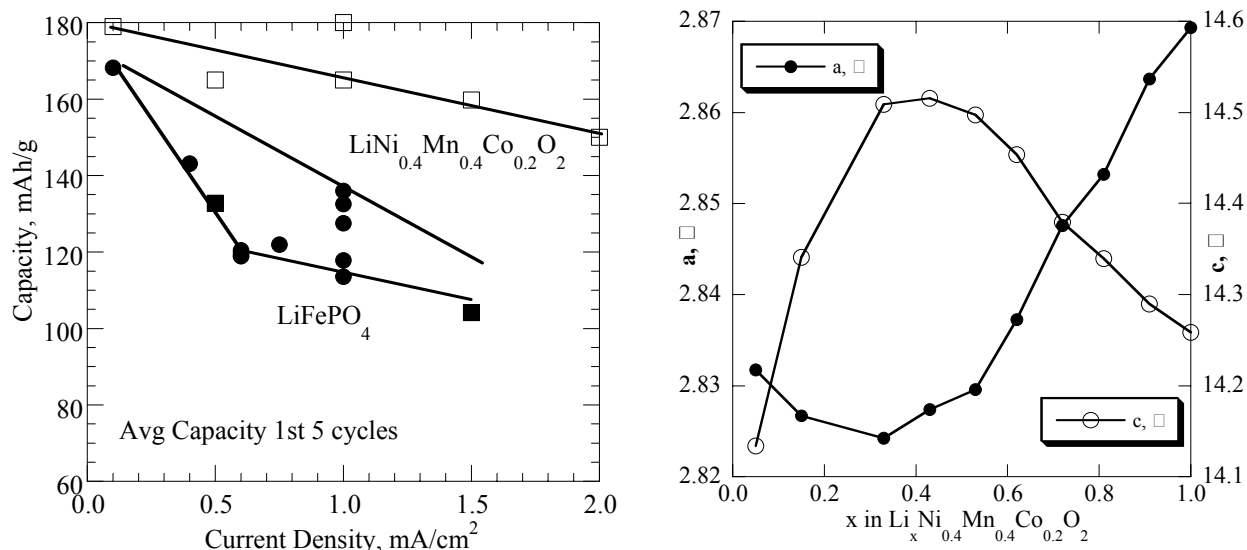


Figure 1. (Left) Cycling capacity of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ as a function of cycling rate compared with LiFePO_4 . (Right) Change of the lattice parameters of $\text{Li}_x\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ as a function of lithium content, during lithium removal.

Further plans to meet or exceed milestones: None

Reason for changes from original milestones: No changes

Publications and Presentations resulting from the work.

- Shoufeng Yang, Yanning Song, Katana Ngala, Peter Y. Zavalij and M. Stanley Whittingham: "Performance of LiFePO_4 as lithium as lithium battery cathode and comparison with manganese and vanadium oxides," *J. Power Sources*. 2003, 119-121: 239-246.
- Yanning Song, Natasha Chernova, Peter Y. Zavalij, and M. Stanley Whittingham: "Iron phosphate and related phases as cathodes for lithium batteries," presented at the Solid State Ionics Meeting in Monterey, July 2003, and in Arcachon, France, September 2003.

TASK STATUS REPORT

PI, INSTITUTION: M. Doeff, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Cathodes - Synthesis and Characterization of Cathode Materials for Rechargeable Lithium and Lithium-Ion Batteries

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To develop low-cost cathodes based on benign materials (*e.g.*, manganese oxides, lithium iron phosphates) having electrochemical characteristics (*e.g.*, cycle life, energy and power densities) consistent with the goals of the USABC and/or PNGV.

APPROACH: Cathode materials are synthesized using both conventional solid-state techniques and solution methods (*e.g.*, sol-gel, glycine-nitrate combustion). The microstructures and atomic structures of the materials are determined by relevant methods, and electrochemical analysis is carried out in a variety of cell configurations. Emphasis is placed on low-cost, structurally stable materials such as manganese oxides and lithium iron phosphate, as well as novel materials with the potential for high energy density.

STATUS OCT. 1, 2002: Initial electrochemical characterization of sol-gel LiFePO_4 samples and O_2 layered manganese oxides will be complete. *In situ* XRD experiments on Li/tunnel MnO_2 cells will be underway.

EXPECTED STATUS SEPT. 30, 2003: Evaluation of Fe-substituted tunnel MnO_2 will be complete. Fundamental studies (*in situ* XRD analysis, diffusion coefficients, thermodynamic measurements, *etc.*) on unsubstituted tunnel MnO_2 will be complete.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES:

- (a) Go/no-go decision on sol-gel LiFePO_4 by April 2003.
- (b) Analysis of *in situ* XRD results on Li/tunnel MnO_2 cells will be complete by September 2003.

PROGRESS TOWARD MILESTONE (a)

A “go” decision was made to continue work on sol-gel LiFePO_4 for purposes of studying the effect of carbon coatings on performance. This synthetic method results in high-purity materials with well-controlled particle sizes, allowing straightforward analysis of the effect of carbon coatings without complications from impurities common to other preparations. We intend to extend our studies to LiFePO_4 and doped variants made by other methods, as well as to other cathode materials once sufficient information about coating variables are obtained.

During the past year, we discovered that LiFePO_4 electrochemical performance was strongly correlated to the structure of surface carbon on the particles, as determined by Raman microprobe spectroscopy (R. Kostecki and F. McLarnon). Coatings with lower D/G (disordered/graphene) and higher sp^2/sp^3 ratios have higher electronic conductivities, and allow better utilization of the LiFePO_4 electrode. By incorporating organic or polymeric additives during synthesis, it is possible to manipulate the D/G and sp^2/sp^3 ratios in the carbon coating. Best results are obtained when small amounts of pyromellitic acid are used. Thermogravimetric analysis (TGA) shows that this compound decomposes rapidly at low temperatures compared to polymeric or polyaromatic compounds (Figure 1). LiFePO_4 samples processed with the latter two also contain residual hydrogen or nitrogen suggesting incomplete decomposition. This is likely to reduce electronic conductivity of carbon significantly.

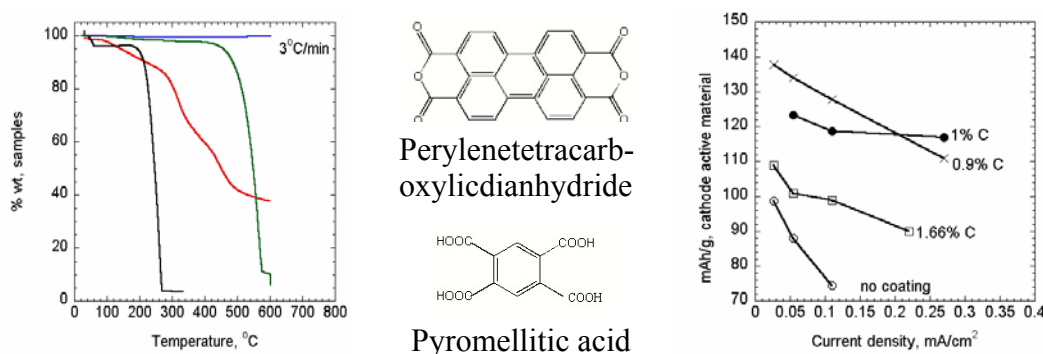


Figure 1 (left): TGA traces of LiFePO_4 (blue), perylenetetracarboxylicdianhydride (green), photoresist polymer (red), and pyromellitic acid (black). Samples were heated at $3^\circ\text{C}/\text{min}$ under N_2 .

Figure 2 (right): Capacity as a function of current density for LiFePO_4 cathodes coated with carbon from pyromellitic acid. An uncoated sample (which contains residual carbon) is shown for comparison.

It is interesting to note that increasing the amount of carbon from pyromellitic acid in the samples does not necessarily result in better performance; best results are obtained when the carbon content is about 1 wt% (Figure 2). Elemental analysis on the sample with 1.66% C indicates some residual hydrogen is present, suggesting that the decomposition rate is dependent upon the amount of pyromellitic acid in the sample. Further work will be directed towards understanding the decomposition pathways of this additive so that coatings can be further optimized.

PUBLICATIONS AND PRESENTATIONS

“Effect of Surface Carbon Structure on the Electrochemical Performance of LiFePO_4 ,” M.M. Doeff, Y. Hu, F. McLarnon and R. Kostecki, **Electrochemical and Solid State Letters**, 6, A207 (2003).

“Evaluation of Sulfur-Doped Aluminum-substituted Manganese Oxide Spinel for Lithium Ion Battery Applications”, M.M. Doeff, J. Hollingsworth, J. Shim, Y.J. Lee, K. Striebel, J.A. Reimer and E.J. Cairns, **J. Electrochem. Soc.**, 150, A1060 (2003).

“A Study of Layered Lithium Manganese Oxide Cathode Materials”, T.A. Eriksson and M.M. Doeff, **J. Power Sources**, 119-120C, 145 (2003).

“Effect of Surface Carbon Structure on Electrochemical Performance of LiFePO_4 ”, M.M. Doeff, R. Kostecki, F. McLarnon, and Y. Hu, **14th International Conference on Solid State Ionics**, Monterey, CA, June 2003, Abstract II O T 02, p. 88.

2) “Investigation of Layered Intergrowth $\text{Li}_x\text{Mn}_{1-y}\text{O}_2$ (M=Ni, Co, Al) Compounds as Positive Electrodes for Li-ion Batteries, M. Dollé, J. Hollingsworth, T. J. Richardson, and M.M. Doeff, **14th International Conference on Solid State Ionics**, Monterey, CA, June 2003, Abstract II O T 13, p. 100.

TASK STATUS REPORT

PI, INSTITUTION: J.B. Goodenough, University of Texas at Austin

TASK TITLE - PROJECT: Cathodes - Novel Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Cost, cycle life, safety, and energy density

OBJECTIVES: To evaluate alternative layered oxides as cathode materials for a Li-ion battery that operates between Ni(II) and Ni(IV).

APPROACH: Layered LiMO_2 oxides have been shown to exhibit a high Li^+ -ion mobility once a fraction of the Li is removed. On the other hand, these oxides are metastable and decompose on upon removal of a large fraction of Li from between the host MO_2 layers. $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ contains Mn(IV) and removal of Li operates on the Ni(III)/Ni(II) and Ni(IV)/Ni(III) couples, both of which are pinned at the top of the $\text{O}^{2-}2\text{p}^6$ band. Ohsuku and Mikimura have demonstrated a capacity over the range 2.5 to 4.3 V vs Li that approaches 150 m Ah/g for 30 charge/discharge cycles at room temperature. We have found that the capacity decreases sharply at higher current densities, which we suspect is the result of poor conductivity. We will investigate (1) whether we can increase the capacity at higher current densities by coating the particles with carbon and (2) the role, if any, of the Mn(IV) ions. Since small particle sizes are probably necessary, sol-gel synthetic routes will be employed.

STATUS OCT. 1, 2002: New project initiated 8/1/02.

EXPECTED STATUS SEPT. 30, 2003: $\text{Li}_2\text{NiMnO}_2$ samples with and without carbon will have been prepared and tested. Preliminary data will have been collected on other materials.

RELEVANT USABC GOALS: 10-year life, < 20% capacity fade over a 10-year period.

MILESTONES: (a) Test the influence of carbon coating on layered and spinel Ni^{2+} , Mn^{4+} compounds operating on $\text{Ni}^{3+}/\text{Ni}^{2+}$ and $\text{Ni}^{4+}/\text{Ni}^{3+}$ couples and assess the role of Mn^{4+} in these compounds. September 30, 2003. (b) Investigation of Mn^{4+} ion by substitution of other M^{4+} ions. January 31, 2003.

PROGRESS TOWARD MILESTONES

- Accomplishments towards milestone over the last quarter.

Evaluation of $\text{Li}_{2-x}\text{NiMnO}_4$

Our initial assessment from XRD data that our strategy for preparing $\text{Li}_2\text{NiMnO}_4$ has yielded a material with few transition-metal ions in the lithium layer has been confirmed by Li-MNR experiments, Fig. 1, that were completed in collaboration with the group of Clare Gray at Stony Brook.

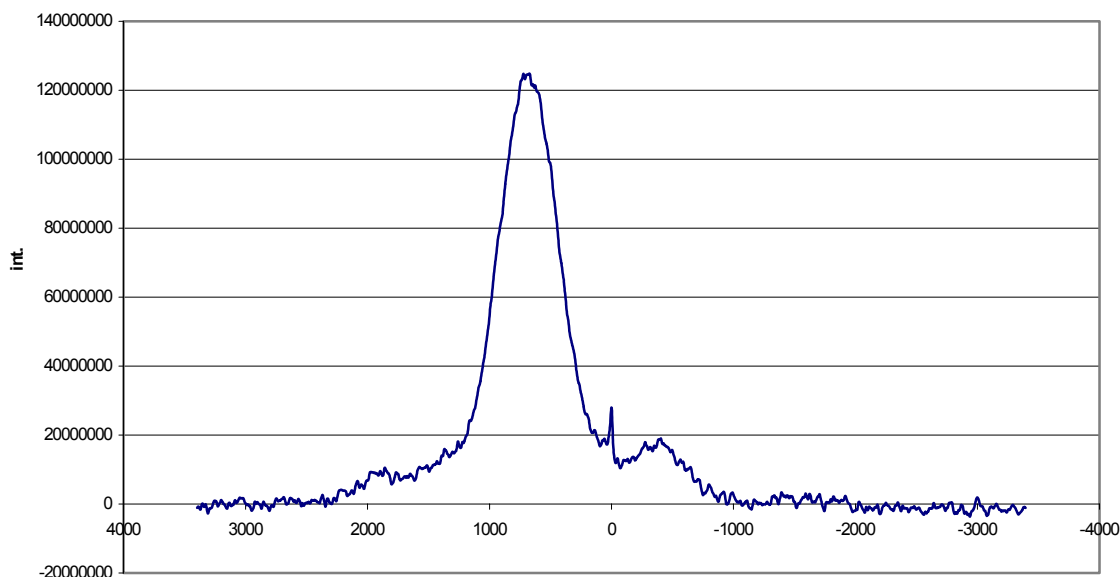
The Ni(III)/Ni(II) and Ni(IV)/Ni(III) redox couples are pinned at the top of the $\text{O}^{2-}2\text{p}^6$ band as antibonding states containing a large admixture of O-2p and Ni-3d orbitals. Electrochemical data show that the Ni(IV)/Ni(III) redox couple is not accessible in $\text{Li}_{2-x}\text{NiMnO}_4$, but it is accessible in $\text{Li}_{1-x}\text{NiO}_2$. This observation implies that there is a stabilization of the Ni(III):3d⁷ level relative to

the O-2p_σ level that increases the ratio O-2p/Ni3d of the admixture of orbitals in the antibonding states as a result of the presence of Mn(IV)-ions. This shift in the energy levels, and therefore in the O-2p/Ni3d admixture ratio, is due to the inductive effect, i.e. a larger covalent component in the Mn(IV)-O bond decreasing the Madelung energy at the neighboring Ni site. In order to access the Ni(IV)/Ni(III) redox couple, it is necessary to go to the smaller values of y in Li_{1-x}Ni_{1-y}Mn_yO₂, which has motivated a comparative study of compositions 0.2 ≤ y ≤ 0.5 in order to obtain a greater capacity. In accordance with our contention that the Ni(III)/Ni(II) and Ni(IV)/Ni(III) are pinned at the top of the O-2p bands, there is no step in the open circuit voltage on crossing from the Ni(III)/Ni(II) to the Ni(IV)/Ni(III) couples. However, initial studies of samples prepared from the oxalates suggest an increasing disorder of transition-metal ions into the Li layers as y decreases in Li_{1-x}Ni_{1-y}Mn_yO₂. On the assumption that this problem is due to reducing atmosphere generated by decomposition of the oxalates, we plan to try synthesis under oxidizing conditions.

Investigation of substitution with M⁴⁺ other than Mn⁴⁺ in LiNi_{1-x}M_xO₂

Our initial investigation has been centered on Ti⁴⁺. Central to obtaining a composition with good electrochemical characteristics is the cation order. In the Ti⁴⁺ system this made more difficult than in the Mn⁴⁺ system due to the larger ionic radii. Matters are further complicated by a very limited number of Ti⁴⁺ precursors that are water solvable and thus suitable for coprecipitation. However, initial attempts using a modified version of the method used in the Li₂MnNiO₄ system have yielded material with intimate mixing of the transition metal cations, a prerequisite for cation ordering at a low temperature. Experiments to deduce the optimal sintering temperature are therefore underway.

LiNi_{0.6}Mn_{0.4}O₂ (⁶Li MAS NMR)
200MHz - spinning rate 35kHz
(Collected by Clare Gray's group at Stony Brook)



- Reason for changes from original milestones: N/A

BATT TASK 5 DIAGNOSTICS

TASK STATUS REPORT

PI, INSTITUTION: R. Kostecki and F. McLarnon, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Electrode Surface Layers

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVE: Establish direct correlations between electrode surface changes, interfacial phenomena, and cell capacity/power decline.

APPROACH: Our approach is to use Raman microscopy, scanning probe microscopy (SPM), ellipsometry, and standard electrochemical methods to characterize cell components taken from baseline BATT Program cells, fresh electrode materials, and thin-film model electrodes. Data to be collected include changes in electrode surface morphology and structure, electrode surface chemistry, and SEI thickness and composition, all of which accompany cell cycle-life tests.

STATUS OCT. 1, 2002: We defined relationships between electrode history, electrode surface properties, and temperature for baseline $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ cathodes. We completed our studies of structural disordering of graphite anodes during cycling at elevated temperatures and correlated the mechanism of SEI reformation upon cycling with graphite structural degradation.

EXPECTED STATUS SEPT. 30, 2003: We expect to develop good understanding of the key elements for good electrochemical performance of LiFePO_4 cathode, *i.e.*, identify the mechanism of electrode degradation in terms of changes of surface morphology and chemistry upon cycling and storage in BATT Program electrolytes. We will identify and confirm material limitations and specific degradation modes. We expect to determine and understand the effects of various synthesis routes, carbon coating, and impurities on the performance of LiFePO_4 cathodes. We will continue to investigate the effect of carbon disordering to determine its impact on long-term Li-ion cell performance. We expect to provide preliminary data from *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials. We plan to provide full diagnostic results for model thin-film LiMn_2O_4 cathodes.

RELEVANT USABC GOALS: 15 year life, < 20% capacity fade over a 10-year period.

MILESTONES: (a) Determine the effect of structure, morphology, carbon coating, and surface impurities on the electrochemical performance of LiFePO_4 electrodes - January 2003.

(b) Develop capabilities to carry out *in situ* Raman spectroscopy and current-sensing atomic force microscopy of individual particles of BATT baseline electrode materials - June 2003.

PROGRESS TOWARD MILESTONES

We used Raman microscopy and current-sensing atomic force microscopy (CSAFM) to detect, monitor and characterize surface phenomena, which occur in the components of baseline BATT Program cells and ATD Program cells. Our first objective during this quarter was to analyze power fade mechanisms of baseline BATT $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ and LiFePO_4 cathodes.

In order to determine a possible impact of the carbon recession on the performance of the composite cathodes we investigated micro-Raman spectra of $\text{LiAl}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$ agglomerates within the color-coded Raman maps of Gen-2 composite cathodes from tested cells. A typical Raman spectrum of a fully discharged composite $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathode is dominated by a broad band centered around $\sim 500\text{ cm}^{-1}$ with a small shoulder at 558 cm^{-1} . On the other hand, Raman spectra of $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ display two clear-cut peaks at 480 and 550 cm^{-1} . By systematically deconvoluting thousands of Raman spectra from $50 \times 80\text{ }\mu\text{m}$ area at $0.9\text{ }\mu\text{m}$ spatial resolution, and integrating the bands characteristic for $\text{Li}_{1-x}\text{Al}_{0.05}\text{Ni}_{0.8}\text{Co}_{0.15}\text{O}_2$, we were able to determine the state of charge (SOC) of individual grains of the active material in the composite cathode. It is worth mentioning here that Raman spectrum of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ active material changes significantly upon application of excessive laser beam power. At intensities $>0.5\text{ mW}$ the broad band at $\sim 500\text{ cm}^{-1}$ converts into one sharp peak at 510 cm^{-1} similar to the spectra of $\text{LiNi}_y\text{Co}_{1-y}\text{O}_2$ reported in the literature.

Interestingly, the cathodes from the room temperature BATT cells, which were assembled and tested by K. Striebel (BATT Task 1) i.e., PG04, PG06 and PG03 displayed spectral variations with location on the cathode surface, which indicate the presence of at least partially charged $\text{Li}_{1-x}\text{Ni}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$. The cathode surface SOC varied between individual grains of active material and, at some locations, the spectra correspond to fully charged material, even though the cell was slowly discharged (C/25) to 3.0 V. However, the surface of the PG13 cathode (cell was cycled at 60°C) consisted of fully charged active material. Fig. 1 shows Raman images of a cathode, which suffered 16% of irreversible capacity loss at the end of the test. It is clear that some particles of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ became electrically disconnected from the remaining part of the cathode due to mechanical stress, carbon additive retreat and poor intergranular electronic contact within $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ agglomerates. Moreover, microprobe Raman spectra from different locations at the surface of the tested cathodes displayed a sharp band at 1009 cm^{-1} accompanied by two sidebands at 642 and 1106 cm^{-1} , which are characteristic for lithium pyrophosphates. There were also areas on the surface of the tested cathodes, which showed very broad and featureless maxima centered around ~ 550 and 1050 cm^{-1} . Their origin is most likely phosphate-type compounds that are products of LiPF_6 decomposition.

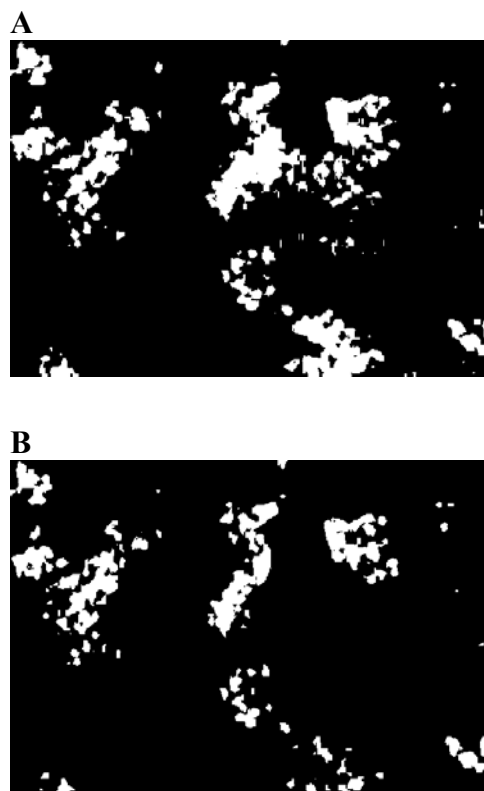


Figure 1. Raman microscopy $50 \times 80\text{ }\mu\text{m}$ surface images of $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ composite cathode from a cell surface. The bright areas show (A) charged and discharged active material, (B) charged active material only.

TASK STATUS REPORT

PI, INSTITUTION: J. McBreen, Brookhaven National Laboratory

TASK TITLE - PROJECT: Diagnostics - Battery Materials: Structure and Characterization

SYSTEMS: High-power Li-ion, high-energy Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: The primary objective is to determine the contributions of electrode materials changes, interfacial phenomena, and electrolyte decomposition to cell capacity and power decline.

APPROACH: Our approach is to use a combination of *in situ* and *ex situ* synchrotron techniques to characterize electrode materials and electrodes taken from baseline BATT Program cells. Techniques that are sensitive to both bulk and surface processes will be used. This will include both K and L-edge x-ray absorption spectroscopy. Exploratory work will be done on other techniques such as non-resonant inelastic x-ray scattering (NRIXS).

STATUS OCT. 1, 2002: We completed extensive *in situ* XRD on LiMn_2O_4 in the 4.1 V region. This included several new findings on the phase behavior and the effect of Li and O stoichiometry on electrode stability. The work also showed that electrolyte composition had major effects on the stability of LiMn_2O_4 at elevated temperatures. Work was also completed on the development of techniques for XAS studies of phosphorous decomposition products in cycled cells, and the techniques was applied to the ATD Program. Structural studies of new high-capacity cathodes and anodes will be ongoing. This includes XAS and XRD work on cathode materials such as LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. Anode work includes XRD on carbon-coated Si and Ge_3N_4 .

EXPECTED STATUS SEPT. 30, 2003: We expect to complete the XAS and XRD work on the cathode materials, LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$, and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$. XRD on carbon-coated Si and Ge_3N_4 will also be completed. Exploratory work on non-resonant inelastic x-ray scattering NRIXS will be initiated. We expect to provide preliminary soft x-ray XAS data on various cathode materials, at the B, F, O, and P K edges and at the L_3 and L_2 edges of the transition metals.

RELEVANT USABC GOALS: 15-year life, <20% capacity fade over a 10-year period.

MILESTONES: (a) Complete *in situ* XAS and XRD studies of LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ by April 2003. (b) Complete *in situ* XAS and XRD studies of Si and nitride-based anode materials by June 2003.

PROGRESS TOWARD MILESTONES

The *in situ* XAS and XRD studies of LiFePO_4 , $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ have been completed. Two papers on the work on $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ have been accepted for publication. The work on the Si and nitride based anode materials has been completed and papers have been published on both. Publications, related to both milestones, are listed below.

1. Won-Sub Yoon, Mahalingam Balasubramanian, Xiao-Qing Yang, Zugen Fu, Daniel A. Fischer, and James McBreen “Soft X-ray Absorption Spectroscopic Study on the $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ Cathode Material during charge” *Journal of the Electrochemical Society*, accepted.
2. Won-Sub Yoon, Clare P. Grey, Mahalingam Balasubramanian, Xiao-Qing Yang, Daniel A. Fischer, and James McBreen “A Combined NMR and XAS Study on the Local Environments and Electronic Structures of the Electrochemically Li-ion deintercalated $\text{LiCo}_{1/3}\text{Ni}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode System” *Electrochemical and Solid-State Letters*, accepted.
3. N. Pereira, M. Balasubramanian, L. Dupont, J. McBreen, L. C. Klein, and G. G. Amatucci, The Electrochemistry of Germanium Nitride with Lithium, *J. Electrochem. Soc.* **150**, A1118 (2003).
4. X. Q. Yang, J. McBreen, W.-S. Yoon, M. Yoshio, H. Wang, F. Fukuda, T. Umeno, “Structural studies of the new carbon-coated silicon anode materials using synchrotron-based *in situ* XRD”, *Electrochemistry Communication*, **4** 893 (2002).

TASK STATUS REPORT

PI, INSTITUTION: P.N. Ross, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics – Interfacial and Reactivity Studies

SYSTEMS: High power Li-ion

BARRIER: Short battery lifetime

OBJECTIVES: The primary objective is to establish direct correlations between electrode surface changes, interfacial phenomena, and cell failure.

APPROACH: Our approach is to use in-situ Fourier transform infrared (FTIR) spectroscopy to study the *interfacial chemistry* in model electrode/electrolyte systems to provide the basis to interpret more complex spectra recorded from ATD Program cell materials. For this year, we will add in-situ differential electrochemical mass spectrometry (DEMS) as a technique for studying *gas generation* from electrolyte decomposition reactions. These spectroscopies will be accompanied by classical electroanalytical methods such as cyclic voltammetry and the rotating ring-disk electrode (RRDE).

STATUS OCT. 1, 2002: Vinylene carbonate added (5 mol%) to PC-based electrolyte was found to prevent graphite exfoliation that normally occurs in PC-based electrolyte. The electrochemical oxidation of the saturated alkylcarbonate solvents used in Li-ion batteries occurs in dry (<20 ppm water) electrolytes only above 5 V. Water added to dry electrolyte causes the oxidation to occur at much lower potentials, e.g., <4 V.

EXPECTED STATUS SEPT. 30, 2003: Determine the oxidative and thermal stability of electrolytes with various electrode materials and impurities, e.g., water. Identify routes to improved stability *via* electrolyte additives and/or electrode pre-treatment.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade over a 10-year period.

MILESTONE: Identify at least one route to improved electrolyte stability *via* electrolyte additives and/or electrode pre-treatment.

PROGRESS TOWARD MILESTONE

The surface films formed on commercial $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ cathodes (ATD Gen2) charged to 3.75V and 4.2V vs. Li/Li^+ in EC:DEC - 1M LiPF_6 were analyzed using ex-situ Fourier transform infrared spectroscopy (FTIR) with the attenuated total reflection (ATR) technique. A surface layer of Li_2CO_3 is present on the virgin cathode, probably from reaction of the active material with air during the cathode preparation procedure. The Li_2CO_3 layer disappeared even after soaking in the electrolyte, indicating that the layer dissolved into the electrolyte possibly even before potential cycling of the electrode. IR features only from the binder (PVdF) and a trace of polyamide from the Al current collector were observed on the surfaces of cathodes charged to below 4.2 V, i.e. no surface species from electrolyte oxidation. Some new IR features were, however, found on the cathode charged to 4.2 V and higher. An electrolyte oxidation product was observed that appeared to contain dicarbonyl anhydride and (poly)ester functionalities. The reaction appears to be an indirect electrochemical oxidation with overcharging (removal of > 0.6 Li ions) destabilizing oxygen in the oxide lattice resulting in oxygen transfer to the solvent molecules.

In collaboration with T.R. Jow's group at the Army Research Laboratory, we studied the formation of the SEI layer on graphite anodes cycled in propylene carbonate (PC) – lithium bis(oxolato)borate (LiBOB) electrolyte using ex-situ Fourier Transform Infrared Spectroscopy (FTIR) analysis in the attenuated total reflection (ATR) mode. The results provide a more-refined description of the composition than earlier analyses with x-ray photoelectron spectroscopy (XPS). The vibrational spectra clearly show that electrochemical reduction of the BOB anion is a part of the SEI formation chemistry. Carboxylate and/or oxalate functional groups derived from the BOB anion were the components assigned as the “semicarbonate” species in the C 1s XPS spectra of the SEI layer formed in LiBOB electrolyte. Reduction of the BOB anion changes the oxygen coordination around the B atom from tetrahedral BO_4 to trigonal BO_3 , e.g. esters of boric acid, and changes the symmetry of the O-C-O bonding closer to that in esters of oxalic acid. Based on the combination of electrochemical and FTIR data, we conclude that the preferential reduction of the BOB anion versus the PC solvent molecule prevents solvent co-intercalation, and is the mechanism responsible for the cyclability of graphite anodes in purely PC-based electrolyte.

TASK STATUS REPORT

PI, INSTITUTION: E.J. Cairns, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Synthesis and Characterization of Electrodes

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Rapid capacity fade

OBJECTIVES: The primary objectives are (1) to directly observe Li in BATT Program cathode materials, (2) characterize the Li atomic and electronic local environment, (3) determine changes in this environment with cycling, and (4) use this information to identify causes of capacity loss and propose improved electrode materials.

APPROACH: Our approach is to use ^7Li MAS-NMR to characterize BATT Program electrodes before and after cycling. Data to be collected are isotropic chemical shift, linewidth, and relaxation times for each species of Li. XRD, magnetic susceptibility, and other data will also be used, as appropriate. NMR data on model failure mechanisms will be used to interpret the spectra. Structural information and information on the local Li environment will be gathered to improve our ability to design new electrode materials. This work will be carried out in collaboration with investigators who prepare and cycle electrode materials (*e.g.*, M. Doeff, K. Striebel, and others).

STATUS, OCT. 1, 2002: We obtained ^7Li MAS NMR spectra for several LiMPO_4 ($\text{M}=\text{Fe}, \text{Ni}, \text{Mn}, \text{Co}$) and $\text{Li}[\text{Mn}_x\text{Fe}_{1-x}]\text{PO}_4$ olivine compounds and established the hyperfine shift mechanism. This information will help elucidate the structural changes during electrochemical cycling. We identified the change in the Ni and Ni-containing environment as a significant mechanism of capacity fade in Gen2 electrodes. We identified the various local environments of Li in the layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials and clarified the correlation between the local environments and electrochemical performance.

EXPECTED STATUS SEPT. 30, 2003: We anticipate that we will have completed an investigation of the capacity fade of several members of the family of layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials. We will also complete our investigation of $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ material in terms of the changes that occur during cycling, and the changes that accompany capacity loss and power loss. We will continue our investigations of the $\text{Li}(\text{Fe},\text{M})\text{PO}_4$ family of materials. As new materials are brought into the program, we will initiate NMR studies of these.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade

MILESTONES: (a) Complete NMR investigation of layered $\text{Li}_y[\text{M}_{0.11}\text{Mn}_{0.89}]\text{O}_2$ materials by August 2003. (b) Complete investigation of the $\text{LiAl}_{0.05}\text{Ni}_{0.80}\text{Co}_{0.15}\text{O}_2$ material in terms of changes that occur during cycling, and changes that accompany capacity and power loss by June 2003.

PROGRESS TOWARDS MILESTONES

Our post-doc, Dr. Young-Joo Lee, has completed her stay at LBNL, and has returned to Korea. All of our results up to the time of her departure were reported at the BATT review in May, 2003.

All milestones have been completed on schedule, and were reported at the review. This work was summarized in the last quarterly report.

NMR studies of Li cell materials will continue under the ATD program, and future results will be reported there.

We currently are interviewing candidates for the post-doctoral position, and expect to issue an offer in the next few weeks.

TASK STATUS REPORT

PI, INSTITUTION: G. Ceder, Massachusetts Institute of Technology
C. Grey, SUNY at Stony Brook

TASK TITLE - PROJECT:..Diagnostics - First-Principles Calculations and NMR Spectroscopy of Cathode Materials with Multiple Electron Transfers per Transition Metal:

SYSTEMS: Cation-doped lithium nickel manganese oxides

BARRIERS: High voltages, low electronic conductivity, stability, and limited electrochemical testing of cathode performance

OBJECTIVES: To engineer high-capacity, stable cathode materials by working with redox-active metal ions that can exchange multiple electrons in a narrow voltage range, focusing initially on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple. Determine the effect of structure and cation doping on the Li deintercalation/ intercalation mechanisms and the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple.

APPROACH: Use solid-state NMR and XAS to characterize local structure and oxidation states as a function of state of charge and number of charge cycles. Use first-principles calculations (density functional theory) to identify redox-active metals, determine the relative stabilities of different structures and the effect of structure on cell voltages, and identify promising cathode materials for BATT Program applications. Use calculations and NMR to identify low-activation-energy pathways for cation migration and to investigate the effect of doping on conductivity.

STATUS OCT. 1, 2002: The analysis of the NMR data for $\text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2$ and $\text{Li}[\text{Li}_{1/9}\text{Ni}_{1/3}\text{Mn}_{5/9}]\text{O}_2$ during the first electrochemical cycle have been completed and compared with results from first-principles calculations. Investigation of multiple-cycled materials by NMR and calculations of the Li_2MnO_3 -NiO phase diagram are on going. Exploratory syntheses of Nb^{5+} -doped systems have been initiated.

EXPECTED STATUS SEPT. 30, 2003: NMR data for $\text{Li}[\text{Li}_{(1-2x)/3}\text{Ni}_x\text{Mn}_{2/3-x/3}]\text{O}_2$ $x = 1/2, 1/3, 1/10$ as a function of charging cycle will have been acquired and the analysis completed. XAS studies of the $x = 1/2$ and $1/3$ samples will be completed. A preliminary phase diagram for Li_2MnO_3 -NiO will have been calculated. Studies of cation doping (e.g., Nb^{5+} , Ti^{4+} , Co^{3+}) on local structure and cell potential will be ongoing. Applications of NMR and calculation methodology to other relevant systems under investigation by members of the BATT Program will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (a) Determine the site energies and voltages of the different Li environments in $(1-x) \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \bullet x \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($M = 4+$) by first-principles calculations. Also determine the Li local environments and nickel oxidation state as a function of state of charge in $(1-x) \text{Li}[\text{Ni}_{0.5}\text{Mn}_{0.5}]\text{O}_2 \bullet x \text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$ ($M = 4+$) by NMR spectroscopy and XAS. (Nov. 2002)
(b) Synthesis and preliminary characterization (powder diffraction and NMR) and electrochemical testing of the Nb^{5+} -doped materials. Perform initial calculations on the effect of cation doping (e.g., Nb^{5+}) on the $\text{Ni}^{2+}/\text{Ni}^{4+}$ couple. Perform (proton and Li) NMR studies of cation locations of iron phosphates and doped lithium (nickel) manganates in collaboration with S. Whittingham (SUNY Binghamton) and M. Thackeray (ANL). Complete XAS studies (with J. McBreen, BNL) of lithium nickel manganates. (May 2003).

PROGRESS TOWARD MILESTONES

Neutron diffraction (ND) experiments have been performed at the Rutherford Laboratory (U.K.) and Synchrotron x-ray diffraction have been collected on samples of $\text{Li}[\text{NiMn}]_{0.5}\text{O}_2$, prepared with different Ni and Li isotopes. Different isotopes were used in the ND experiments to allow more accurate determinations of multiple site occupancies, and local structure to be probed with pair distribution function (PDF) analysis methods. The PDF experiments contain sufficiently high resolution that the different M-O and M-M bond lengths can be resolved. Experiments at Los Alamos are scheduled (November 2003) and the samples of charged $\text{Li}[\text{NiMn}]_{0.5}\text{O}_2$ (to approx. 50% and 90% of the theoretical capacity) have been prepared. Synchrotron XRD data have been collected for the $x = 0.5$ sample. A sample of $\text{Li}[\text{NiTi}]_{0.5}\text{O}_2$ has been synthesized by ion exchange and will be partially charged and prepared for neutron diffraction with the objective of investigating possible cation migration after charging. These results, together with the computational work, will give further insights into which transition metal ions are susceptible to migration upon electrode cycling.

Samples of $\text{Li}[\text{NiMn}]_{0.5}\text{O}_2$ have been investigated with TEM studies, performed in collaboration with Y. Shao-Horn (MIT); TEM analysis is complete for the $x = 1/2$ sample. Results indicate the formation of an unusual $\sqrt{3} \times \sqrt{3}$ superstructure. Studies of the $x = 1/3$ sample are underway. Charged samples will also be examined. First principles calculations have indicated that the Li-Ni disorder is critical in explaining this superstructure, but no definite ordering scheme has yet been found. The first principles model is being extended to account for the disorder observed in TEM.

NMR studies have been performed on a limited number of cycled samples, which show noticeable structural changes with cycling. A larger more complete study is now underway, which includes a study of the effect of cycling at high and low voltages on cathode structure. ^2H -enriched electrolytes will be examined for evidence of electrolyte decomposition and proton/deuterium insertion into the cathode materials. Variable-temperature studies are underway to explore the effect of temperature on electronic conductivity, ion mobility and on cathode structure (for partially charged samples) at elevated temperatures.

Interactions with other members of the BATT program (M. Thackeray, S. Whittingham and J. Goodenough) are ongoing.

TASK STATUS REPORT

PI, INSTITUTION: T. Devine, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Diagnostics - Corrosion of Current Collectors

SYSTEMS: Low-cost Li-ion

BARRIER: Uncertain and possibly inadequate corrosion resistance of Al current collectors

OBJECTIVES: Characterize the long-term corrosion performance of Al current collectors in Gen 2 chemistry baseline cells. Determine the mechanism of passivation in Gen 2 electrolyte and identify the passive film responsible for the corrosion resistance of Al current collectors in Gen 2 cells. Identify electrolytes of multi-component salts that are optimized for battery service and that are noncorrosive to Al current collectors.

APPROACH: Inspect for corrosion damage the Al current collectors taken from the many tens or hundreds of batteries that have been life-tested following a well-defined testing protocol. ATD Program cells are the most likely source of data. Analyze by Extreme Value Statistics the results of the failure analyses and predict 10-yr and 15-yr performance of Al current collectors in Li-ion batteries. Use a combination of electrochemical tests (anodic and cathodic polarization and concurrent measurement of mass change using electrochemical quartz crystal microbalance; electrochemical impedance spectroscopy) and surface analytical techniques (optical and scanning electron microscopy, energy dispersive x-ray analyses and Raman spectroscopy) to investigate the mechanism of corrosion and passivation of Al in baseline electrolyte and in other electrolytes relevant to Li-ion batteries (*i.e.*, electrolytes of multi-component salts that are noncorrosive and are optimized for battery service).

STATUS OCT. 1, 2002: Life-tested batteries that are to be autopsied for corrosion-related damage of current collectors have been identified and grouped according to the identities of the electrolytes, cathode materials, and testing protocol. Inspection of the current collectors from life-tested batteries has begun. Preliminary electrochemical experiments to investigate passive film formation on Al in Gen 2 electrolyte has been completed.

EXPECTED STATUS SEPT. 30, 2003: Characterization of the performance of Al current collectors in life-tested batteries will be complete. The 10-yr and 15-yr performances of Al current collectors in Gen 2 electrolyte will be calculated using Extreme Value Statistical Analyses. The accuracy of the predictions will be a function of the quantity and quality of the data acquired from the failure analyses. The mechanism of Al passivation in Gen 2 electrolyte will be determined. The mechanism of Al passivation in electrolytes of multi-component, non-corrosive salts will be well underway.

RELEVANT USABC GOALS: 10-year life, <20% capacity fade.

MILESTONES:

- (a) 10-year and 15-year performance of Al current collectors in Gen 2 batteries will be predicted based on Extreme Value Statistical Analyses of life-tested cells by August 2003.
- (b) Mechanism of Al passivation in Gen 2 electrolyte will be determined by August 2003.

PROGRESS TOWARD MILESTONES

To predict the corrosion-related lifetime of aluminum current collectors, the extent of corrosion was measured in batteries that were assembled and tested by other researchers at LBNL. Specifically, aluminum current collectors were removed from two types of Li-ion batteries: “coin cells,” which had been tested by Dr. Marca Doeff, and “ATD batteries,” which had been tested by Dr. Kathy Striebel. Corrosion of the aluminum current collectors was detected by a combination of optical and scanning electron microscopies. In all instances, the form of corrosion was pitting corrosion. The extent of corrosion was measured by the number of pits, the depth of each pit, and the area of the aluminum surface covered by corrosion pits. Unfortunately, significant mechanical damage that is indistinguishable from pitting corrosion occurred during the assembly of the ATD batteries. As a result, lifetime predictions are based on the corrosion behavior of the current collectors of the coin cells.

Two different cathodes, LiFePO_4 and LiMn_2O_4 , were used in the coin cells, which employed a lithium anode and an electrolyte of 1M LiPF_6 in EC+DMC. A total of 36 current collectors from coin cells were inspected. Corrosion was detected in 33 of the 36 collectors. Dr. Doeff tested the coin cells by cyclically charging and discharging at one of three different current densities: 0.013 mA/cm^2 , 0.27 mA/cm^2 and 0.05 mA/cm^2 . The same amount of charge was passed during each cycle for the different values of current densities. Thus, the time of discharge for tests at 0.13 mA/cm^2 was approximately twice as long as the discharge time for tests at 0.27 mA/cm^2 . In cells with LiFePO_4 cathodes, the amount of corrosion varied inversely with the magnitude of the current density. Stated differently, the amount of corrosion varied directly with the time of charging. For cells with cathodes of LiMn_2O_4 , the opposite was true. The amount of corrosion varied directly with the current density. These results suggest that different corrosion mechanisms operate on current collectors covered with LiMn_2O_4 and with LiFePO_4 . The most severe corrosion occurred in collectors covered by LiMn_2O_4 collectors and subjected to a total of 80 charge/discharge cycles. However, the highest rate of corrosion damage occurred in collectors with LiFePO_4 cathodes and subjected to 10 charge/discharge cycles. The results predict that corrosion of current collectors with LiMn_2O_4 cathodes would cause a 20% decrease in capacity of the battery after 1,000 cycles of 0.1 mA/cm^2 .

To determine the mechanism of passivation of aluminum in battery electrolytes, two types of experiments were conducted: electrochemical anodic polarization tests in which the corrosion rate of aluminum is measured as a function potential, and IR and Raman spectroscopies of the solid corrosion products formed on samples of anodically polarized aluminum. Most interestingly, the results of the anodic polarization tests indicate that the corrosion of aluminum is related to the compositional purity of the aluminum and the solvent. High-purity aluminum is very resistant to pitting corrosion in EC+DMC, but low-purity aluminum undergoes severe pitting corrosion. If the purity of the EC is lowered from 99.9% to 99.0%, high-purity aluminum is susceptible to pitting corrosion. Finally, far IR spectroscopy of the surface of aluminum anodically polarized in 1.2 M LiPF_6 with a solvent of EC + DMC indicates the corrosion resistance of aluminum is most likely due to the formation of a protective film that consists, in part, of AlF_3 .

BATT TASK 6 MODELING

TASK STATUS REPORT

PI, INSTITUTION: J. Newman, Lawrence Berkeley National Laboratory

TASK TITLE - PROJECT: Modeling - Improved Electrochemical Models

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIERS: Side reactions, dendrite formation, low capacity, safety

OBJECTIVES: Develop experimental and computational methods for measuring and predicting transport, kinetic, and thermodynamic properties. Model electrochemical systems to optimize performance, identify limiting factors, and mitigate failure mechanisms.

APPROACH: Develop model of dendrite formation on Li metal. Use simulations to improve understanding of the SEI layer. Use simulations to understand performance limitations of baseline BATT chemistries and to identify promising design options.

STATUS OCT. 1, 2002: Analysis of the effect of side reactions on measurements of transport properties is completed. Molecular-dynamics simulations of diffusion coefficients in multicomponent electrolytes such as LiPF_6 in EC:DMC will be nearing completion. Diagnostic experiments of the SEI layer on lithium-tin electrodes are completed. Modeling of dendrite growth and initiation will be ongoing. Modeling of the SEI layer will be ongoing. Modeling the performance of baseline BATT chemistries LiFePO_4 and $\text{Li}_{0.4}\text{MnO}_2$ will be in progress. A preliminary model to describe the concentration and voltage profiles in polymer laminates will be completed.

EXPECTED STATUS SEPT. 30, 2003: Molecular dynamics simulations of diffusion coefficients will be completed. Modeling dendrite initiation in viscous and elastic electrolytes will be ongoing. Comparison of SEI simulations with experimental results and refinement of the model will be ongoing. Modeling of the performance limitations of LiFePO_4 will be completed, and modeling of other BATT baseline chemistries will be ongoing. Simulation of the behavior of conductive polymers for overcharge protection will be completed. The model for the behavior of polymer laminates will be completed and compared to experimental data.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, <20% capacity fade.

MILESTONES:

1. Develop model of electronically conducting polymers for overcharge protection by May 1, 2003.
2. Model of LiFePO_4 and determination of performance limitations by August 1, 2003.

PROGRESS TOWARD MILESTONES

MILESTONE 1:

This was completed and has been reported on in a previous quarterly report.

MILESTONE 2:

Over the last three quarters, we have developed a model for the phase change and diffusion in the iron phosphate electrode, compared the model to experimental data, and identified the performance-limiting factors. Ohmic drops due to the poor conductivity of the active material and transport limitations in the solid phase were identified to be the cause for the low rate capability of this chemistry. The cathode model was integrated into a cell model with a natural graphite anode to simulate the baseline and identify the optimum design in order to maximize the specific energy of the battery. The specific energy maximization was conducted for a wide range of discharge times, ranging from 2 mins to 10 hours, in order to capture both EV and HEV needs. This resulted in a map of the maximum performance of this baseline chemistry, allowing us to gauge its ability to achieve the DOE goals. While achieving the DOE energy goals (150 Wh/kg) was seen to be possible, achieving the power goals appear to be more challenging. The thickness and porosities identified using this optimization procedure have been provided to the Cell Development group (Kathy Striebel).

OTHER PROGRESS

Past theories of electrode stability assume that surface-tension forces counter the amplification of surface roughness at cathodes, and have shown that at lithium/liquid interfaces, the instability cannot be prevented. Last quarter, we treated interfacial stability in lithium/polymer systems where the electrolyte is solid. Linear elasticity theory was employed to compute the effects of bulk mechanical forces in addition to surface tension. The lithium and polymer were treated as Hookean elastic, characterized by their shear moduli and Poisson's ratios, and stress distributions were computed in the electrode and electrolyte phases. These results are necessary to determine regimes of electrode stability.

A model of the solid electrolyte interface (SEI) layer has been developed to understand how transport through the SEI layer affects battery operation. Simulations have been run at different charging rates to examine the effect of current density on the ohmic and charge transfer resistances of the SEI. New film-formation mechanisms will be reviewed and implemented in the coming months.

Previous attempts at transference-number measurement were limited in accuracy by side reactions and the inability to solve independently for activity coefficient and transference number values. New experimental methods are being developed to avoid these issues. To avoid side reactions, a negative electrode of a more moderate potential than lithium is being investigated. This negative electrode is reversible to lithium ions; when paired with a positive electrode reversible to anions in the electrolyte, activity coefficients can be measured independently. Experiments began in a beaker-type cell; however, electrode instability and a high ohmic resistance led to the choice of a three-electrode swagelok cell for further experiments. Improved transport-property measurement will assist in modeling of baseline chemistries.

TASK STATUS REPORT

PI, INSTITUTION: A.M. Sastry, University of Michigan

TASK TITLE - PROJECT: Modeling and Experimentation – Electrochemical Materials

SYSTEMS: Li/polymer and low-cost Li-ion

BARRIER: Short lithium battery lifetimes

OBJECTIVES: Predict the role of conductive and mechanical failures on reduced performance in the baseline systems, by tightly coupled experimental and simulation studies of microscale transport and mechanics phenomena.

APPROACH: Use simulations to design combinations of conductive additives to improve battery performance, and specifically reduce irreversible capacity losses (ICL). Perform complete studies of electrode (both anode and cathode) conduction, with cell testing to confirm the materials' effect on battery performance. Show improvement in performance of baseline materials with strategic additives, as determined by simulation.

STATUS OCT. 1, 2002: Confirm structure/function relationships in carbon additives in baseline systems. Determine effect of lamination on contact resistance in baseline systems. Determine initial relationship between ICL and conductivity of anode. Initiate testing of cathodes. Initiate simulations of cathode conductivity.

EXPECTED STATUS SEPT. 30, 2003: Experiments (LBNL and UM) and simulations on conduction in baseline anodes and cathodes, with correlations developed relating material composition and cell capacity losses will be completed. Modeling of other BATT Program baseline chemistries will be ongoing.

RELEVANT USABC GOALS: Specific power 300 W/kg, 10 year life, < 20% capacity fade

MILESTONES: (a) Determine relationship of ICL to electrode conductivities by May 2003.
(b) Carry out simulations of conduction in cathodes with experimental verification by June 2003.

PROGRESS TOWARD MILESTONES

Accomplishments toward milestone over last quarter

Thin, multilayered electrodes were fabricated with carbon additives to reduce resistive losses between current collector and active materials (Striebel), in order to verify new experimental techniques and analytical models for conduction. Progress has been made on development of an analytical solution to conduction in multilayered sheets; it is likely that an analytical solution may be derived, to obviate the need for direct, finite element simulations. These would prove far more useful/tractable for other DOE researchers, and are being pursued vigorously. As part of this analysis, resistive losses at the interfaces are also being investigated.

Maximum depth-to-particle-dimension ratios in which systems can be treated as two-dimensional, rather than three-dimensional systems in determining percolative properties were studied. This problem is of great technological significance, since three-dimensional solutions for percolation in even low-density systems pose much more intensive computational problems than their two-dimensional analogs, and also result in significantly different predictions for percolation onset. We have systematically investigated the effect of particle shapes and arrangements on percolation properties which would have important implication for developing high energy density / high power density of battery and can be used by other teams to design electrodes.

Numerical codes for data reduction four-point-probe experimental data on two-layered electrodes were equipped with a user-friendly graphical user interface (GUI) to ease their application by other DOE researchers (initially, Striebel and co-workers).

• Further plans to meet or exceed milestone

We will continue to provide all codes for analysis of multilayered electrodes to other DOE workers, and plan to integrate new materials manufactured by Striebel into our theoretical studies, both as validation of models, and in order to continue to provide guidance on selection/design of materials.

• Reason for changes from original milestone: N/A

BATTERIES FOR ADVANCED TRANSPORTATION TECHNOLOGIES (BATT)
QUARTERLY REPORT FOR JULY – SEPTEMBER 2003
CALENDAR OF UPCOMING EVENTS

June 2003

- 1 - 6 1st International Conference on Polymer Batteries and Fuel Cells (PBFC-1) – Jeju Island, Korea (Conference Headquarters Office, Department of Chemical and Biomolecular Engineering, KAIST, 373-1, Guseong-dong, Yuseong-gu, Daejeon, 305-701, KOREA; 82-42-869-3925; fax: 82-42-869-3910; pbfc@pbfc.kaist.ac.kr; <http://pbfc.kaist.ac.kr>)
- 22 - 27 14th International Solid State Ionics Meeting - Monterey, CA (Turgut Gur, Stanford University, turgut@stanford.edu; <http://www.ssi-14.net/>), Asilomar

August 2003

- 31 – Sept. 5 54th ISE – Florianopolis, Brazil (Prof. L.A. Avaca)

September 2003

- 17 – 20 High Energy Density Electrochemical Power Sources – Nice, France (Marcelle Gaune-Escard, HEDEPTS 2003, Polytech'Marseille, IUSTI, 5 rue Enrico Fermi, 13453 Marseille cedex 13, France; 33 4 91 10 68 82; fax: 33 4 91 11 74 39; email: battery@polytech.univ-mrs.fr; <http://iusti.univ-mrs.fr/HEDES2003/index/html>)

October 2003

- 12 - 17 204th Electrochemical Society Meeting – Orlando, FL (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

March 2004

- 7 - 10 First International Seminar on Fuel Cell Development and Deployment, Program Chairman, Nigel Sammes, University of Connecticut, School of Engineering, 44 Weaver Road Unit 5233, Storrs, CT 06269, Tel: 860.486.9204, Fax: 860.486.8378, E-mail: sammes@engr.uconn.edu. (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2004

- 9 - 14 205th Electrochemical Society Meeting – San Antonio, TX (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

June 2004

- 1 - 4 4th International Advanced Automotive Battery Conference (AABC-04) – San Francisco, CA (530-692-0140; fax: 530-692-0142); AAABC04@advancedautobat.com – <http://www.advancedautobat.com/aabc.html>; The Renaissance Parc 55

27 – July 2 12th International Meeting on Lithium Batteries, IMLB12 – Nara, Japan (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; imlb12@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

September 2004

19 - 24 55th Annual Meeting of the International Society of Electrochemistry – Thessaloniki, Greece (Prof. E. Theodoridou) <http://www.isechemistry.gr/>

October 2004

3 - 8 206th Electrochemical Society Meeting – Honolulu, HI (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2005

15 - 20 207th Electrochemical Society Meeting – Quebec City, Canada (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; <http://www.icmcb.u-bordeaux.fr/libd>)

September 2005

25 - 30 56th Annual Meeting of the International Society of Electrochemistry – Busan, Korea (Contact: H Kim; hasuckim@plaza.snu.ac.kr)

October 2005

16 - 21 208th Electrochemical Society Meeting – Los Angeles, CA (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

May 2006

7 - 12 209th Electrochemical Society Meeting – Denver, CO (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)

23 - 29 Lithium Battery Discussion Meeting, LiBD2004 – Arcachon France (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; email: Josh.Thomas@mkem.uu.se; <http://www.icmcb.u-bordeaux.fr/libd>)

October 2006

29 - Nov. 3 210th Electrochemical Society Meeting – Cancun, Mexico (The Electrochemical Society Inc., 10 South Main Street, Pennington, NJ 08534-2896; (609) 737-1902, fax: (609) 737-2743; ecs@electrochem.org; <http://www.electrochem.org/meetings/meetings.htm>)